

QUANTIFICATION OF HYDROGEN CYANIDE GENERATED AT LOW
TEMPERATURE O-CHLOROBENZYLIDENE MALONONITRILE (CS) DISPERSAL

by

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Thesis submitted to the Faculty of the
PMB Graduate Program
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In partial fulfillment of the requirements for the degree of
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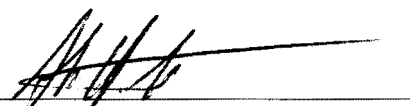


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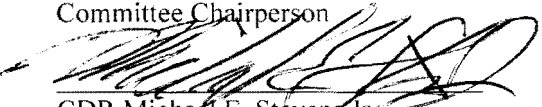
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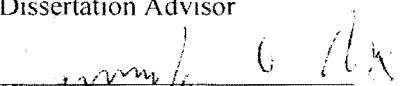

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DEDICATION

This thesis is dedicated to Edgar, my husband, and my two children Eli and Elin. Without their love and support, the completion of this research would not have been possible.

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ABSTRACT

Quantification of Hydrogen Cyanide Generated at Low Temperature O-Chlorobenzylidene malononitrile (CS) Dispersal

Erin Johnson-Kanapathy, MSPH, 2013

Thesis directed by: Michael Stevens, Ph.D., Department of Preventive Medicine and Biometrics

Hydrogen cyanide (HCN) is an acutely toxic airborne chemical compound [Immediately Dangerous to Life or Health (IDLH) 50 parts per million (ppm)] and has been previously determined to be a thermal degradation by-product of the riot control agent o-chlorobenzylidene malononitrile (CS). Previous research and studies conducted by U.S. Army and Air Force in mask confidence chambers demonstrated quantifiable airborne HCN levels released into the atmosphere at CS combustion temperatures of 350 to ~800°C. Presently, many CS confidence chambers exist in the military for training purposes and CS thermal combustion (aerosolization) processes are known to vary widely amongst these different sites. As such, the combustion temperature achieved may be impacted, and thus, the airborne concentration of HCN generated may be impacted, creating a potentially higher or lower HCN level depending on the combustion temperature. Given this procedural variability, this study focused on determining the range of combustion temperatures in which HCN is generated. Particular focus centered on identifying if HCN is generated at combustion temperatures as low as 100 °C and if

the levels quantified exceed established occupational exposure limits (OEL), such as the NIOSH Recommended Exposure Level (REL)-Short Term Exposure Limit (STEL) of 4.7 ppm, and Military Exposure Guidelines (MEGs). This study quantified airborne HCN levels generated in both the field, at live CS training events at Ft. Jackson, SC, and in the laboratory using a tube furnace operated at discrete CS combustion temperatures over a range of 100 °C to 350 °C. Study findings indicate that HCN is quantifiable even at 100 °C, much lower than previously hypothesized, but well below the OEL and MEGs. Findings may assist in standardizing DoD doctrinal policies related to thermal combustion processes within CS chambers.

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CHAPTER 1: Introduction

BACKGROUND

O-Chlorobenzylidene malononitrile, $C_{10}H_5ClN_2$, (CS) was first developed in 1928 by two scientists in Great Britain, Corson and Stoughton, but it was not until 1959 that CS was adopted as the U.S. Army's riot control agent (RCA) of choice, replacing chloroacetophenone.(35) In comparison to chloroacetophenone, CS was found to have a lower threshold of incapacitation [5 milligrams per cubic meter (mg/m^3) for CS and 35 mg/m^3 for chloroacetophenone], greater speed of symptom onset, lower toxicity (estimated lethal dose for CS $60 \times 10^3 \text{ mg min}/m^3$ and $10 \times 10^3 \text{ mg min}/m^3$ for chloroacetophenone), less damage to eyes, and a decrease in severe contact dermatitis.(19) Over 50 years later, CS is still used by civilian law enforcement as a riot control agent and in the military as both a riot control agent and a training aid for the use of the currently used military gas mask, the M40 Protective Mask.(35)

CS is an effective irritant and lachrymator that produces a stinging/burning sensation on exposed skin, heavy production of nasal and sinus mucous, salivation, coughing, and intense burning sensation of the eyes at what is considered training concentrations of $1\text{-}3 \text{ mg}/m^3$ [0.9-2.7 parts per million (ppm)].(2) Higher levels of exposure [$5\text{-}10 \text{ mg}/m^3$ (4.5-9 ppm)] may produce nausea, vomiting, and increased irritation of skin in addition to the aforementioned effects. The effects of CS exposure continue until removal from contaminated atmosphere and generally resolves after 10 minutes of exposure to fresh air.(2) One aspect of the use of training concentrations of CS is that in normal, healthy persons the effects are temporary. However, in the case of persons that are affected by asthma, high blood pressure, cardiovascular problems, lung

congestion and even a common cold, they can experience an increase in adverse effects and recovery time may increase.(2)

In military mask confidence training exercises, CS is vaporized by heat (methods such as propane burners, hotplates, and oxidizing candles are used to generate the heat for CS combustion) followed by condensation to an aerosol and assisted in dispersal through the chamber by fans.(35) CS is also able to be dispersed using pyrotechnic mixtures in burning grenades.(2) Within the last decade, there has been an increase in interest and concern over the airborne concentration of CS and the thermally generated CS by-products during training exercises, as indicated by an increase in research within this area of interest.(16; 17; 20; 21; 35) An impetus for this increased attention on chamber safety stemmed from an incident where two young officers died from cardiac related issues shortly after participating in a mask confidence chamber exercise.(41)

Subsequent to this incident, research had hypothesized and found potentially harmful thermal degradation products at predicted and non-predicted temperatures.(16; 20; 21) Some of the CS by-products that are formed during the thermal aerosolization of CS have been previously determined and include potentially harmful compounds such as HCN and malononitrile.(12; 14; 16; 20; 21; 23; 31) These by-products may be more hazardous than CS, depending on concentration and exposure duration. Previous research has explored several areas of this problem, with focus on temperature ranges of CS dispersal. Qualitative analysis of the compounds that are formed during high temperature CS dispersal (>300 °C) has been conducted. In addition, quantification of CS high temperature dispersal by-products such as hydrogen cyanide (HCN) has also been performed for dispersal temperatures greater than 350 °C.(14; 20; 21) Efforts

researching by-products created as a result of relatively low temperature (<300 °C) CS dispersal by Hout *et al.* have also been performed.(16; 17)

Combined qualitative results from Hout *et al.* (<300 °C) and Kluchinsky *et al.* (>300 °C) indicated at least 17 different compounds being identified as produced within a range of 150-750 °C.(16; 20) Of these compounds identified, HCN is a significant compound of human health concern due to its acute toxicity (estimated human LC50 is 546 ppm at 10 minutes of continuous exposure).(5)

While the temperature threshold of several by-products generated has been investigated and identified, HCN is still unknown. Knowledge of HCN and these other thermal degradation by-products of CS and the quantification of exposure have both military and law enforcement relevance. From a military standpoint, every soldier must go through an initial mask confidence chamber exercise to meet basic training requirements and then must periodically complete chamber training at various time intervals throughout their respective military careers. Personnel in certain occupational specialties conduct the training on a more regular, frequent basis for longer duration of exposure than what other military personnel would be exposed.(2-4; 7; 18) While there are general required procedures which are implemented at each training site (such as the amount of CS capsules used), differences in the temperature of CS dispersal (sites may combust CS below the researched temperatures of ≥ 350 °C) and specific procedures vary (such as the heating instrument).(2-4; 7; 18) The field sampling portion of this study occurred at Fort Jackson, SC, an Army basic training base, which used a low temperature of CS dispersal (200 °C).

RESEARCH OBJECTIVES

This research focused on the production of HCN at low temperature CS dispersal, specifically on determining the low temperature threshold in which the CS degradation by-product, HCN, is generated during CS thermal dispersal, as well as the quantification of HCN over a range of relatively low CS combustion temperatures in the laboratory. Additionally, to characterize the potential airborne HCN exposure risk to Soldiers, the quantification results of HCN samples taken within the Ft. Jackson, SC chamber and their respective times of exposure were compared to published human health guidelines. These guidelines included the U.S. Army Public Health Center's Military Exposure Guidelines (MEGs)(39), the Environmental Protection Agency's (EPA) Acute Exposure Guideline Levels (AEGLs)(40), the National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL)-Short Term Exposure Level (STEL)(27), along with the American Conference of Government Industrial Hygienists (ACGIH) Ceiling Limits(5). A desired benefit of this study would include the determination of a temperature range of CS dispersal which would generate airborne levels of HCN well below these established occupational exposure limits.

Aim #1

Quantify HCN during U.S. Army Mask Confidence Training exercises at Ft. Jackson, SC, a primary training base for the U.S. Army basic trainees, to provide "real world" observations of HCN concentrations at low temperature CS dispersal (<350 °C) within an actual CS training chamber.

Aim #2

Determine the airborne concentrations of HCN generated when utilizing a commercially available tube furnace over a range of relatively low dispersal temperatures

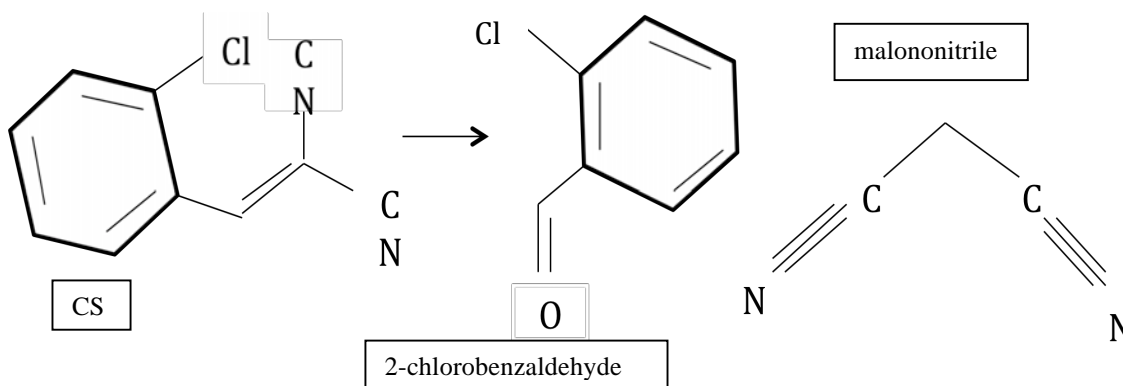
for CS. The temperature range used for the tube furnace experiment have not been previously investigated (100-350 °C).

CHAPTER 2: Literature Review

CHEMICAL PROPERTIES AND HEALTH EFFECTS

O-chlorobenzylidene malononitrile is a yellowish, crystalline semi-volatile organic compound containing two cyanide compounds that has a melting point of 95 °C, and a vapor pressure of 3.4×10^{-5} mm Hg at 20 °C. When dissolved, CS is rapidly hydrolyzed to o-chlorobenzaldehyde and malononitrile (see Figure 2-1). The further degradation of malononitrile may lead to the formation of HCN.(35) When CS is employed as an aerosol, the persistence in the air is dependent upon air movement (stagnant air flow will cause the particulates to remain in the air longer than if there is an air current).(2) Once the CS particulates come in contact with a surface, they adhere and generally will not re-aerosolize.(2) While there are several formula variations to CS that impact its persistency in the environment (such as CS1 and CS2) and how it is disseminated in the environment (such as CSX), the focus of this research is the primary formulation known simply as CS, as this is the formulation that is used for training.(2)

Figure 2- 1: CS hydrolyzed to malononitrile and 2-chlorobenzaldehyde



CS has known acute effects on skin, eyes and the respiratory system; creating a stinging/burning of skin, severe burning sensation of the eyes, copious quantities of mucous generated in the nose and sinus cavities, coughing, dyspnea, and chest tightness at levels around 1-3 mg/m³ (0.9-2.7 ppm) (this concentration range is considered to be the level recommended for training concentrations per Department of the Army Field Manual 3-11.11 Flame, Riot Control, and Herbicide Operations).(2; 35) The National Institute of Health's (NIH) TOXNET database also notes cardiovascular, gastrointestinal, renal, and hepatic effects.(24) While these effects may occur at higher levels of exposure, sensitive individuals (for example those with preexisting conditions such as respiratory and cardiovascular conditions) may experience the more severe effects even at lower concentrations than 1-3 mg/m³ (0.9-2.7 ppm).(2) The Occupational Safety and Health Administration (OSHA) has set an 8 hour Time Weighted Average (TWA) of 0.05 ppm (0.39 mg/m³) based upon eye and skin irritation and the Immediately Dangerous to Health and Life level was set at 2 mg/m³ (0.26 ppm) based upon studies conducted by Punte *et al.* that demonstrated that the majority of exposed humans would not be able to tolerate levels in excess of 2-10 mg/m³ (0.26-1.3 ppm) for 2 minutes of exposure.(9; 10; 33) The Threshold Limit Value-Ceiling (TLV-C) of 0.05 ppm (0.39 mg/m³) was developed by the American Conference of Governmental Industrial Hygienists (ACGIH) to address and minimize eye and respiratory tract irritation, dermal sensitizations, headaches, and prevent respiratory epithelium damage.(6) Increases in humidity and temperature creates an increased effect on the skin, potentially from an increase in rate of hydrolysis and opening of pores on the skin creating an increase in surface area of skin exposed; an important note to consider when evaluating military training dermal

exposures.(33) In military mask confidence training exercises, CS is vaporized by heat followed by condensation to an aerosol and assisted in dispersal through the chamber by fans.(35) It is this heat dispersal that serves as a catalyst for the formation of by-products.(20)

Hydrogen cyanide is a thermal degradation by-product of CS and is a low molecular weight, volatile, colorless gas with a vapor density of 0.941 and vapor pressure of 630 mm Hg at 20 °C (see Figure 2-2).(5; 8) HCN has a faint bitter almond odor that not all persons can detect.(5) Volatilization is significant for the degradation of HCN from surfaces and soil. While highly diffusive when in the atmosphere, HCN slowly degrades (1.4-2.9 years atmospheric half-life and is resistant to photolysis) and can potentially be transported long distances from the source of emission before reacting with hydroxyl radicals. Dry and wet deposition is a negligible pathway for removal from the atmosphere for HCN, but cyanide particles may be removed by those pathways.(8)

Figure 2-2: Hydrogen Cyanide



Hydrogen cyanide can rapidly act as a metabolic asphyxiant, inhibiting cytochrome oxidase, thus preventing cellular respiration, leading to histiotoxic hypoxia. HCN can have systemic effects such as cardiac, dermatologic, neurologic and endocrine effects.(8; 28; 30; 36; 38; 39) Acute effects of exposure to TLV-C levels of HCN include cardiac irregularities, dermatologic effects, and nervous system effects. Coma and death

can occur with exposure to high concentrations (LC50 of 546 ppm at 10 minutes of continuous exposure). The primary routes of entry for occupational exposures are inhalation and dermal absorption, with inhalation having a greater rate of absorption than dermal exposure.(5; 8; 28; 30; 32; 36; 38; 39) Some of HCN physical effects are similar to symptoms from CS exposure to include respiratory tract irritation, headaches and nausea.(5; 6) This is important to note with concurrent exposures with the thermal dispersal of CS which may impede the determination of the potential source of symptoms that are experienced.

While the acute effects of HCN are of primary concern when investigating HCN as a thermal degradation product of CS during military training events, it is worthwhile to note chronic low level exposure effects. The basis for the NIOSH REL-STEL of 4.7ppm was based primarily on study that looked at chronic low level exposures in an occupational setting.(5) The study conducted by El Ghawabi *et al.*, looked at workers with an average of seven years exposure in a concentration exposure range of 4.2-12.4 ppm. The researchers noted that the symptoms such as throat irritation, vomiting, salivation, dyspnea, headache, weakness, taste/smell changes, nervous instability, lacrimation and thyroid enlargement were greater in the exposed population than the control.(5; 13) Another study conducted by Chandra *et al.* investigated chronic exposure concentrations of 0.18-0.72 ppm. The researchers found that the workers presented with complaints of signs/symptoms of HCN poisoning. Of note, no other chemicals were reported/investigated and correlation between chronic effects and HCN exposure was not reported.(5; 11)

PREVIOUS RESEARCH ON HCN GENERATION FROM CS COMBUSTION

A few years after the military began using CS as a riot control/training agent research into the chemical's degradation products began. The first research noted was in 1961, as Porter *et al.* conducted research into pyrolytic decomposition of CS in an oxygen environment and found the liberation of detectable levels of cyanide at 595 °C and 615 °C.(31) A decade later, continuing with the research into decomposition products of CS, McNamara (1971) looked at the possibility of cyanide poisoning in the case of fire in a CS storage area. In his research, McNamara looked at the overall percentage of HCN obtained in relation to amount of CS combusted. He was able to obtain 0.003% HCN, burning raw CS, and up to 0.25% HCN, burning raw CS mixed with Napalm B. These percentages were significantly less than the 28% HCN predicted based on the chemical formula (the two CN molecules make up to 28% of the molecular weight of CS).(23) This signified that CS when burned, generated less HCN than predicted (possibly from other breakdown products and recombination) and demonstrated that the higher temperature of CS pyrolysis generated a higher percentage of HCN. From the 1970's to the early 2000's, research into HCN as a thermal degradation product of CS stalled.

In 2001, as response to an incident where two young officers died from cardiac related issues the same day after participating in a mask confidence chamber exercise, the Fort Knox, Kentucky Industrial Hygiene Office conducted CS and HCN sampling inside the mask confidence chamber. A propane camp stove was used to combust the CS, and while the temperature of thermal combustion was not recorded, the authors estimated that the propane and air mix flame temperature reached levels as high as 1,967 °C. During the Fort Knox study two static HCN air samples, utilizing NIOSH Method 7904, and one bulk sample from the floor for cyanide, unknown analysis method, were taken. The

duration of the static air samples were 54 minutes and 14 minutes. All samples for HCN/cyanide were found to be below detection level of $1.0 \mu\text{g}/\text{m}^3$ (0.0009 ppm) but the authors hypothesized that this might be due to recombination of HCN with other compounds that have been formed.(41)

Research into CS concentrations during high temperature dispersal and its degradation products by Kluchinsky and associates began at the Uniformed Services University (Bethesda, MD), shortly after the industrial hygiene survey was conducted at Fort Knox, investigating thermal degradation by-products of CS at high temperature of dispersal. Specifically, Kluchinsky *et al.* quantitatively investigated if HCN is formed during high temperature dispersal of CS. Using two Type 3 CS canisters, CS was dispersed at a temperatures exceeding 700°C in a Riot Control Agent Training Chamber (RCA) (room volume of 240m^3). Four 15 minute air samples were collected for analysis of HCN using NIOSH Method 7904 (total volume air analyzed 14.94-15.98 L) and an additional two 3 minute 18 second samples were collected, at a later date, for analysis by NIOSH Method 6010 (total volume air analyzed 1.66-1.68 L). Results indicated that HCN concentrations ranged from 3.9-5.4 ppm (NIOSH Method 7904) to 10-15 ppm (NIOSH Method 6010). The results approached or exceeded the ACGIH Ceiling/NIOSH REL-STEL of 4.7 ppm.(20)

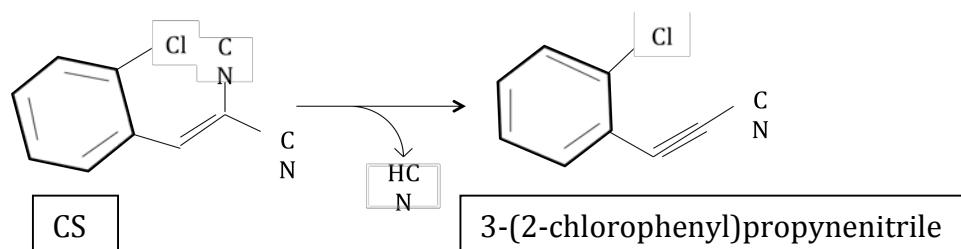
In a separate study, Gutch *et al.* investigated multiple forms of benzylidene malononitrile compounds, with a focus on the chlorine substituted form (CS). Two experiments were conducted to research thermal degradation products from these compounds. The first experiment conducted flash vacuum thermolysis in a glass assembly with analytical grade CS at intervals within reaction temperature between 300-

600 °C with a 30 second contact time. HCN was quantified using a spectrophotometric method. This study showed that chlorinated benzyldene malononitrile was potentially stable up to 300 °C and completely decomposed by 600 °C. HCN was determined to be one of the major gas products formed. HCN was found starting at 350 °C. The percent of HCN was determined to increase with the increase in temperature. The second experiment used thermogravimetric analysis in a nitrogen atmosphere for decomposition of CS. Gutch *et al.* found that CS had a decomposition range of 125-225 °C using this method. They hypothesized that the difference in range of decomposition was potentially due to the recombination of radicals which would prolong decomposition.(14)

While most previous research focused on high temperatures of CS dispersal (>300 °C), Hout *et al.* followed up on the Kluchinsky *et al.* research by investigating low temperature dispersal of CS (150-300 °C) and the thermal degradation products that are formed. The follow-on research on the thermal degradation by-products was conducted in a RCA training chamber during a mock up of a training exercise (mock training exercise is when the policies and procedures are replicated but does not involve the variables, such as durations and procedure deviations, that may occur with live training exercises with Soldiers). CS powder from two capsules was aerosolized using an oxidizing candle as the heat source, producing a measured combustion temperature of 275 °C. Solid phase microextraction (SPME), a simple and solventless method for sample collection and injection for gas chromatography, was the collection method used to passively collect airborne degradation by-products and gas chromatography/mass spectrometry (GC/MS) for qualitative analysis. Additionally, a tube furnace experiment in a laboratory setting was used to examine thermal degradation by-products at increasing

temperatures of CS generation from 150-300 °C. One CS capsule was burned for each sample collected. SPME with GC/MS analysis was utilized to qualitatively determine degradation by-products. From the tube furnace experiment results, a hypothesis that HCN is generated at approximately 275 °C was formed. This hypothesis was generated due to the presence an indicator compound, 3-(2-chlorophenyl) propynenitrile (a CS thermal degradation by-product), which suggests the loss of a CN molecule from the parent compound (Figure 2-3).(16) While the presence of HCN below 300 °C was hypothesized to occur, quantitative analysis of HCN at temperatures lower than 300 °C is still a research area that needs to be investigated.

Figure 2-3 CS degraded to 3-(2-chlorophenyl) propynenitrile



Based on research conducted by Hout *et al.*, the 559th Aerospace Medicine Squadron (AMDS) Bioenvironmental Engineering (BE) Flight conducted personal air sampling in the Mask Confidence Chamber, specifically focused on the thermal degradation by-products from thermal CS dispersal. Four samples for hydrogen cyanide were evaluated using NIOSH Method 6010. Exact duration and volume of sample was not noted but it was stated that the CS gas exposure was approximately 27-34 minutes in duration. This chamber used a propane-powered burner at high setting and combusted 1

CS capsule on an iron skillet initially, with an additional capsule per each group that entered the chamber. The burner produced a measured temperature range of 350-700 °C. Results for hydrogen cyanide ranged from 0.14 ppm to 0.18 ppm, well below the ACGIH Ceiling/NIOSH REL-STEL of 4.7 ppm. (12) Similar to previous studies that quantified HCN, the temperature of dispersal was in excess of 300 °C. Of important note is that the amount of CS used was significantly less than what is currently used in Army Mask Confidence Chambers (volume of the room in which CS was employed for the IH survey was not noted).

A preliminary study conducted by Hout *et al.* qualitatively investigating the presence of HCN was conducted based upon the presence 3-(2-chlorophenyl) propynenitrile at 275 °C. Utilizing a commercially available tube furnace (Barnstead-Thermolyne, Dubuque, Iowa), CS was combusted within a temperature range of 150-300 °C and the aerosolized CS sampled at 25 °C intervals. Nitrogen gas was utilized as the flow gas at a rate of 475-500 ml/min. After three minutes of the CS being exposed to the heat, a SPME fiber with a Carbowax/Divinylbenzene (CW/DVB) fiber coating was inserted into a sampling port and exposed for two minutes to the aerosolized CS. This process was repeated in triplicate. Samples were then analyzed via GC/MS with a Plot-Q column. At each temperature point, starting from 300 °C and extending down to 150 °C, HCN was detected. An additional part of the preliminary study used a direct reading instrument known as the Multi Rae (RAE Systems, San Jose, California) during mock chamber that combusted CS at 275 °C. HCN was detected at 1 ppm with 1 capsule combusted and 3 ppm with 2 capsules combusted. HCN was also detected qualitatively within the mock chamber using SPME and GC/MS analysis.(15)

The question of whether or not HCN is present in detectable quantities, using NIOSH methods, during low temperature dispersal of CS in live training exercises and the temperature threshold for generation has not been investigated. Table 2-1 provides an overview of previous research. With the varying methods of CS dispersal having a wide range of dispersal temperatures, knowledge of this emission range of HCN can lead to enhanced safety protocols within Army confidence chamber doctrine, preventing unnecessary exposures.

Table 2-1: Previous Research Overview

Area	Porter	McNamara	Army	Gutch	Kluchinsky	Hout	Air Force	Kanapathy
Low Temp. <300°C						X		X
High Temp.> 300°C	X	X	X	X	X		X	X
Quantification		X	X				X	X
NIOSH Method			X		X	X	X	X
SPME						X		X
Mock Training					X	X		
Live Training			X				X	X
Laboratory	X	X		X		X		X

Overview of previous and current research detailing HCN as a thermal degradation product of CS. Highlighted areas of research note this study's core area of focus. Mock training is a replication of training exercises using the same policies and procedures without the presence of Soldiers who are training, eliminating various variables that may occur during live training exercises. Live training exercises occur when Soldiers are conducting training and the researchers are in an "observer" mode.

CHAPTER 3: Methods and Materials

CHAMBER REGULATIONS

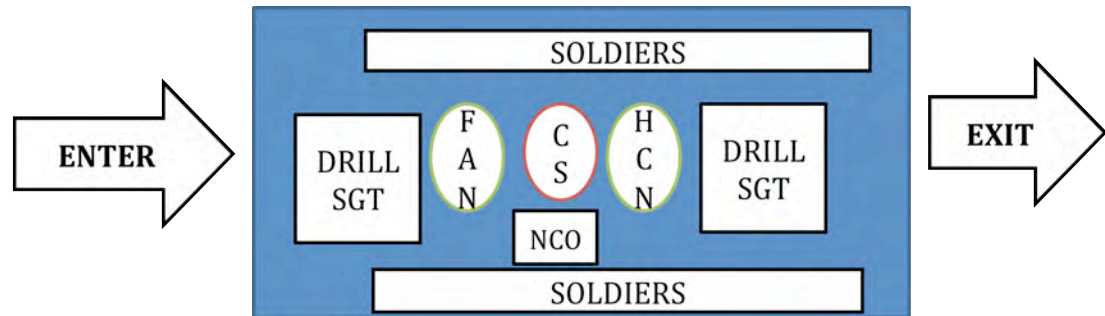
Current Army regulation limits the use of RCAs in training to using only CS (capsule form only during chamber exercises). Additionally, CS is not to be employed in ways that are dangerous to life and/or property.⁽⁴⁾ Per the chamber exercise instructions [Training Support Package (TSP) 805-B-2040 Chemical, Biological, Radiological, and Nuclear (CBRN) Defense 2], the standard of the exercise is to operate within a chemical environment by performing the following in order: stay within the chemical environment for two minutes without adjusting the M40 mask, then when given the command each Soldier is to, within nine seconds, break the seal of his/her respective mask and then seal/clear it again, then for an additional one minute remain in the chemical environment while masked, and lastly, remove the mask and immediately exit from the chemical environment. This procedure is to ensure the Soldiers are able to properly wear and use the mask along with understanding that the mask is working in the chemical environment (thus providing them with “confidence” in the use and function of their mask). Materials listed in the Training Support Package to be used by the instructors for any Army Confidence Chamber are 34 CS capsules, hot plate or oxidizing candle (which may generate different temperatures than the hot plate), a candle lighting device, a coffee can (to place the CS powder into on top of the heat source), the M40 Protective Mask, and the chemical protective uniform. The students’ (Soldiers’) material list includes the M40 Protective Mask, chemical protective uniform (uniform that is worn over the ACU), and their tactical field gear.⁽³⁾ One capsule per 30 cubic meter (m^3) is to be dispersed for initial chamber concentration and an additional capsule dispersed per 10 personnel that

go through the chamber.(7) Prior to entry into the chamber, all masks are to be inspected for fit and function. If a Soldier's mask does not properly fit or function they will receive a new mask or use another Soldier's mask after that Soldier has completed the chamber exercise. Individuals that have medical reasons for not entering the chamber will be identified and not conduct the chamber exercise. Contact lenses are not to be worn inside the chamber to prevent CS particulates from being trapped in between the contact lens and the eye (eyeglass inserts for the protective mask are issued to Soldiers). After the initial administration and pre-exercise checks are completed, Soldiers will then enter the chamber.(3) Upon exiting the chamber with the mask removed, the Soldiers will walk around in a "decontamination" track (area away from non-exposed personnel) until the CS effects subside.(3) The Department of the Army Pamphlet 385-63, entitled Range Safety (Chapter 13, Chemical Agents and Smoke) states that unprotected personnel will not be exposed to RCAs greater than 15 seconds and prescribes the use of personal protective equipment for Army personnel who handle or dispense CS (protective mask with hood rubber boots, and field clothing secured at ankles, wrist and neck).(4)

OBSERVED MASK CONFIDENCE CHAMBER EXERCISE PROCEDURE

While knowledge of the written policies and procedures for the Army is important, the actual chamber exercise procedures are vital to understanding the route of exposure. At Fort Jackson, SC, one to three companies conducted this training daily Monday through Saturday. While this was the case, each individual basic training recruit typically participates in the chamber exercise only one time during their basic training experience, for a brief period.

Figure 3-1 Chamber Layout



Basic layout of chamber. Soldiers participating in the exercise line up along the walls. Drill Sergeants work in the center of the chamber. The CS Generation site is located centrally inside the chamber with the CBRNE NCO standing beside it. A large fan is used to help direct the aerosolized CS. The HCN sample point was located ~5 feet from the CS generation point.

Soldier Grouping (Companies and Platoons) and Chamber Description

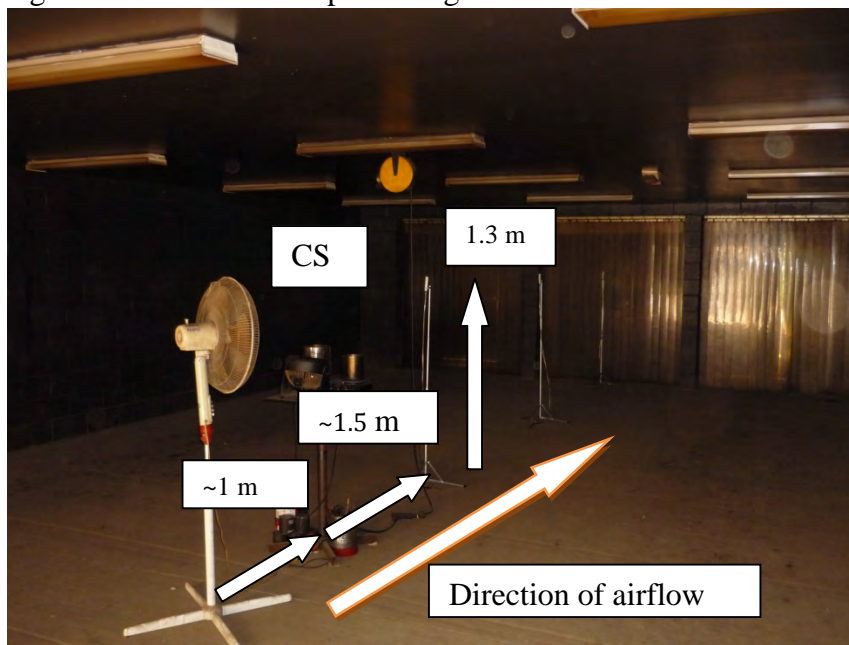
Each company consisted of four platoons, with 45-64 Soldiers in each platoon (180-240 Soldiers in a company). Each company had approximately eight Drill Sergeants (DS). The DS stayed in the chamber throughout the training exercise. During the chamber exercise, a Chemical Biological Radiological Nuclear and Explosives (CBRNE) Noncommissioned Officer (NCO) dispersed the CS and was present during the duration of training (~60 minutes per company). The CBRNE NCO (supervisor) was generally assigned to manage the chamber for all companies conducting training throughout the day. There were ~3 CBRNE NCOs that would alternate conducting chambers throughout the week. There was potential for an individual CBRNE NCO to

conduct multiple chambers within a day and a week. The standard personnel protective equipment (PPE) worn by personnel entering the chamber that had CS combusting was an air-purifying M40 protective mask (ILC Dover, Frederica, Delaware), which is a military equivalent of the commercially available Millenium full-face air-purifying respirator (Mine Safety Appliances, Cranberry Township, Pennsylvania). The chamber was 43 feet (13.11m) long by 24 feet (7.32m) wide by 10 feet (3.05m) high for a total of 10,320 ft³ (293 m³).

Exposure Source

At Fort Jackson, SC, aerosolized CS was generated in the center of the chamber using a hot plate as the heating agent, as indicated in Figures 3-1 and 3-2. A coffee can was placed on top of the hot plate (set on highest setting), paper was torn up and placed inside the coffee can (Figure 3-3) and the CS capsules are opened up and the granules are dispersed into the torn paper (Figures 3-4 and 3-5). A small fan was used by the CBRNE NCO intermediately to direct the flow of aerosolized CS (Figures 3-6 and 3-7). A large fan was placed approximately three feet from the CS generator to direct the flow of CS towards the Soldiers. The chamber was initially “charged” with ten CS capsules, ten to twenty minutes prior to the entry of the Soldiers (the CBRNE NCO and the D.S. were in the chamber during this time) followed by six CS capsules as each platoon entered and conducted the exercise. The doors to the chamber remained closed during the exercise, except when the platoons entered and exited. The chamber was not purged until all companies that were scheduled for the day had completed the chamber exercise.

Figure 3-2 Chamber Setup Looking “Downwind” Towards Exit



Chamber setup showing fan, CS dispersal point, and air sample points for HCN (1st pole to the right of CS dispersal point), and CS (at all three poles).

Figure 3-3 Coffee Can on Hotplate



Paper is torn up and placed inside the coffee can atop the hotplate.

Figure 3-4 CS Capsules



CS capsules staged for charging the chamber and recharge for 1st group of Soldiers.

Figure 3-5 CS Placed Into Coffee Can



CS capsules being opened and emptied into coffee can on hot plate.

Figure 3-6 CS Hand Held Fan



CS capsule contents combusted to aerosolize CS.

Figure 3-7 CS Hand Held Fan Dispersal



CS being blown by hand held fan.

Chamber Exercise (Route of Exposure)

One platoon entered the chamber at a time and remained inside the chamber for approximately ten minutes (Figures 3-8 and 3-9). The Soldiers lined up along the lengthwise sides of the chamber (Figure 3-10). The D.S. freely moved throughout the chamber. During this time the Soldiers were instructed to complete a series of exercises to include running in place, head movements, and chewing to test the fit of their respective masks (Figure 3-11). The D.S. instructed the Soldiers to break the seal of their masks and state their full names and identification number then had them reseal and clear their masks. In groups of ten Soldiers, the platoons were then instructed to remove their masks completely, place the masks back into the mask carrier that was around their waists, and state the Soldier's Creed (Figures 3-12 and 3-13). This last exercise lasted between 17-128 seconds, varying depending on reaction of the Soldiers to the exercise. At the conclusion of this exercise the Soldiers exited the chamber (Figure 3-14). Personal exposures to airborne concentrations of aerosolized CS and HCN varied from Soldier to Soldier due to these variations.

Figure 3-8 Chamber Entry Preparation



Soldiers preparing to line up for entry into the chamber.

Figure 3-9 Chamber Entry



Soldiers waiting to enter into the chamber with protective masks on.

Figure 3-10 Initial Line Up Inside Chamber



Soldiers lined up inside of chamber performing mask seal confirmatory tasks (nodding head, chewing, running in place, etc).

Figure 3-11 Instruction of Chamber Exercise to Soldiers



Soldiers receiving instruction for the next step in the chamber exercise.

Figure 3-12 Preparation for Mask Removal



Soldiers lining up to prepare to remove masks.

Figure 3-13 Mask Removal



Soldiers remove masks and recite the Soldier's Creed prior to exiting the chamber. Note the immediate physical reactions to the CS.

Figure 3-14 Chamber Exit



Soldiers exiting chamber with masks off.

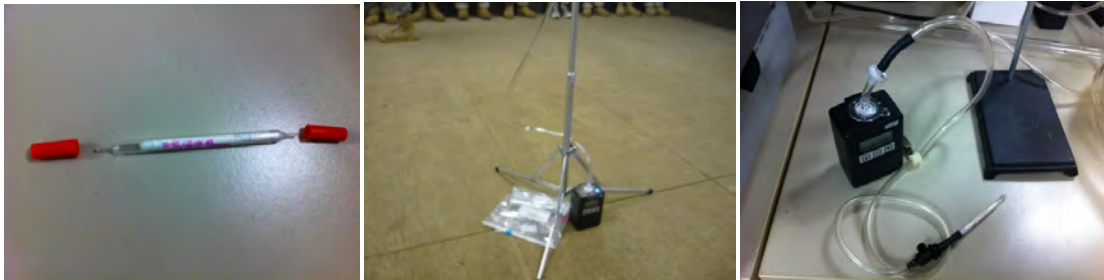
CHAMBER SAMPLING

As this research represented an observational study to document and characterize CS exposure, no changes or suggestions for change were made by the researchers

regarding to any chamber procedures which took place during this research. This method allowed for “real time” sampling to occur with the variability that may occur in a non-controlled setting (such as amount of CS combusted and duration of sampling/exercise). A Hotmux thermal datalogger (DCC Corporation, Pennsauken, New Jersey) was used to determine temperature generated from hotplate that was used for CS dispersal. At a recorded 200 °C, this temperature is lower than past recorded temperatures using different combustion methods (i.e. oxidizing candles, propane burner).(12; 15; 20; 41) NIOSH Method 6010 was used to quantify HCN levels at fifteen minute intervals and training exercise duration (~60 minutes) during a three week period in August and September 2012. NIOSH Method 6010 is more sensitive with less interference than NIOSH Method 7904, an alternative method for HCN sampling.(27)

The NIOSH Method 6010 sample consisted of a solid sorbent tube of 600mg/200mg soda lime connected to personnel air sampling pumps (Figure 3-15 and 3-16). HCN is adsorbed onto the soda lime sorbent and particulate cyanide is captured on the front glass fiber membrane disk.(27) For this experiment, the maximum flow rate of ~200-ml/min was used to obtain the largest possible volume. After each sampling period, each sorbent tube was removed from the pump, capped and sealed in individual plastic bags, and then placed into an ice filled cooler. HCN samples were shipped to the U.S. Army Public Health Command (USAPHC) and subsequently shipped to a contract laboratory for analysis less than one week from each sample drawn. Analysis was performed via a visible spectrophotometer (Thermo Genesys 20, Thermo Scientific, Waltham, Massachusetts) using a modified NIOSH Method 6010. A 4-point calibration curve was performed by the laboratory for quantitative purposes.

Figure 3-15 Sample Train



From left to right: soda lime sorbent tube, personal sampling pump with tubing next to pole used to hold sample in place, complete sampling train.

Figure 3-16 Sample Set Up In Confidence Chamber



HCN sample placed on first stand to the left of the CS generation point.

A static sampling pump (Airchek XR5000, SKC, Eighty Four, Pennsylvania) was placed five feet downwind of the CS combustion station as indicated in Figure 3-1 and Figure 3-16, to represent Soldiers' exposure. This location was chosen to capture exposure without interfering with training. Every fifteen minutes during the exercise the sorbent tube was changed out for a new sorbent tube. A total of four 15 minute samples per company were taken times fourteen companies for a total of 56 samples. Sample

placement and duration were determined by a pilot study conducted July 2012 that examined variability of exercise and feasibility of sample locations.(18)

Exercise duration samples to characterize supervisor exposure were placed on each of the CBRNE NCO with the pump in their respective pocket and each respective sorbent tube clipped to the lapel of the uniform in the individual's breathing zone. The sampling pump was turned on when CBRNE NCO entered the chamber and then turned off when CBRNE NCO exited the chamber. Time of sampling ranged from 40-92 minutes. One sorbent tube per company was used for each exercise duration sample. A total of eighteen supervisory samples were collected and analyzed.

During the three week period, three consecutive training exercise samples (two companies conducting chamber exercise on same day) were taken as the opportunity arose. A static sampling pump was positioned next to the CBRNE NCO. These samples were started from the start of the first company training exercise of the day and were ended after the completion of the subsequent company's training exercise. Sample duration ranged from 102-401 minutes.

An additional eight 15-minute samples and two CBRNE NCO samples, using NIOSH Method 6010, were taken concurrently with samples that were sent to APHC. These samples were sent to and were funded by the Navy & Marine Corps Public Health Center Consolidated Industrial Hygiene Laboratory (CIHL) Detachment Norfolk for comparison. After receipt by CIHL, the samples were then sent to a contract laboratory for analysis. Analysis was performed via spectrophotometer/visible absorption (HACH DR5000, HACH, Loveland, California) in accordance with NIOSH Method 6010 (no method modifications). Table 3-1 provides an overview of quantity of samples taken.

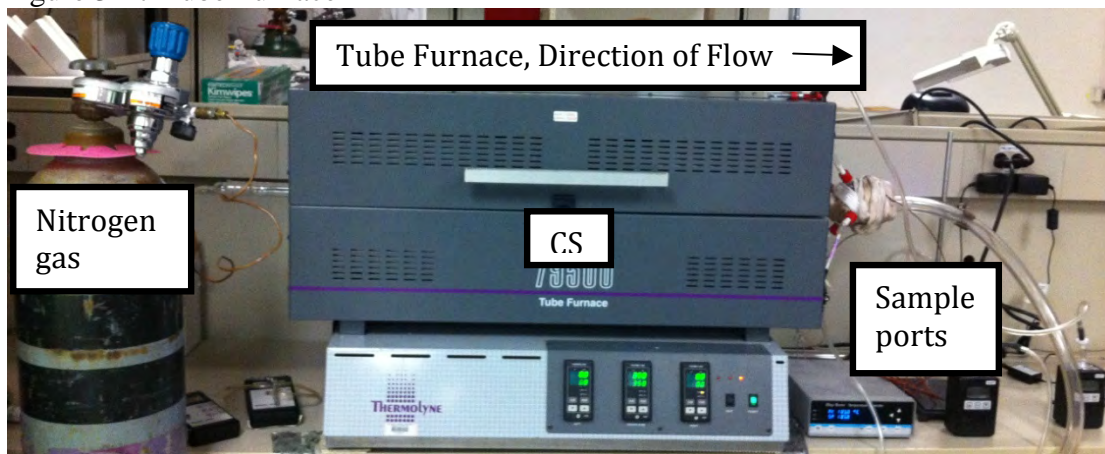
Table 3-1 Overview Sample Size

LOQ 2.7 µg		LOQ 1.1 µg	
Sample	n	Sample	n
15 minute	56	15 minute	8
Supervisor	18	Supervisor	2
Consecutive Exercise	3	N/A	N/A
Total	77	Total	10

A sample size of eighteen was calculated to be sufficient to estimate the mean concentration for the supervisor samples with a margin of error of 0.4973 based on a 95%, 2-sided confidence interval. A sample size of fifty-six was calculated to be sufficient to estimate the mean concentration for the 15 minute samples with a margin of error of 0.2678 based on a 95%, 2-sided confidence interval. A sample size of three was calculated, post hoc, to be sufficient to estimate the mean concentration of the consecutive samples with a margin of error of 2.484 based on a 95%, 2-sided confidence interval. Sample size was calculated based on analysis of the confidence interval for one mean.(22)

TUBE FURNACE

Figure 3-17 Tube Furnace



Nitrogen gas enters from the left flowing to the right. Sample introduced from left side and pushed to center of tube furnace glass tube. Samples collected on the right side of the tube furnace. Exhaust flows out to laboratory ventilation hood.

In a laboratory setting, utilizing a commercially available tube furnace (Barnstead-Thermolyne, Dubuque, Iowa) (Figure 3-17), different quantities of HCN that were generated at a range of temperatures were measured, using NIOSH Method 6010.

Quantitative Analysis

To capture lower range of temperatures of CS dispersal that had not been previously investigated, the temperature range of 100-350 °C at 25 °C intervals was used for quantitative sample collection points. Test runs were conducted to determine the duration that one CS capsule takes to combust, which was determined to be ~2-2.5 hours, and to determine the most effective nitrogen flow rate (~425-475 ml/min). Nitrogen gas was chosen for the inert flow gas based on previous research and to minimize reactions, such as oxidation.(16) While an inert gas was used to assist in flow, the tube furnace experiment was not conducted in a “true” closed system. Ambient air was introduced

each time a capsule was added to the system along with air entry from the exhaust side; more gas is pulled out by the static air sampling pumps (600 ml/min) than is entered into the reaction tube (~450 ml/min). One CS capsule (average weight 0.64 grams) was emptied on to a combustion boat and inserted into the center of the tube furnace quartz reaction tube using a metal rod. Three capsules total were used, inserted at evenly spaced time intervals. The total air volume sampled ranged between +/- 10% of 90L, NIOSH recommended maximum volume, with higher volumes collected for the lower portion of the temperature range to ensure adequate volume captured to obtain results above LOQ. Nitrogen flow gas was set at 350-450 ml/min to prevent backpressure and assist in flow of aerosolized CS. Three static sampling pumps (Airchek XR5000, SKC, Eighty Four, Pennsylvania) with 600mg/200mg soda lime sorbent tubes set at a flow rate of 200ml/min each, running concurrently, were used for the sample collection.

After each sampling period, each sorbent tube was removed from the pump, capped and sealed in plastic bags, and placed in a refrigerator until shipped to the laboratory. The HCN samples were shipped to USAPHC and subsequently shipped to a contract laboratory for analysis less than one week from each sample drawn (per NIOSH Method 6010 samples are stable up to two weeks).(27) Analysis was performed via a visible spectrophotometer (Thermo Genesys 20, Thermo Scientific, Waltham, Massachusetts) using a modified NIOSH Method 6010.

A total of eleven sample points within the temperature range was determined to be sufficient to provide an 80% power with a 5% significance level and detectable beta[j] (meaningful regression coefficient) of 0.61. Sample size was calculated based on linear regression analysis. (22)

Analysis Methods

For both objectives, concentration means (along with 95% Confidence Intervals) were calculated and compared to established exposure guidelines. Regression analysis was also conducted for the laboratory analysis to assess the relationship between the concentration of HCN and the temperature of CS combustion. To determine whether or not there was a correlation between temperature and concentration, Pearson's Correlation Coefficient was calculated for normal distribution and Spearman's Correlation Coefficient for non-normal distribution. For the case of a large quantity of censored data within a small sample set, confidence intervals for the results were analyzed as proportions (samples quantified over total samples taken) using the modified Wald method. In the case of when a small proportion of censored data, $\frac{1}{2}$ of the reporting limit was used.

CHAPTER 4: Results

CHAMBER

Overview Results

A total of 56 samples of 15-minute duration and a total of 18 supervisor/CBRNE NCO samples (lasting between 40-92 minutes) were sent to USAPHC for analysis. All 74 samples were below the limit of quantification (LOQ), $LOQ < 2.7 \mu\text{g}$, for vapor HCN. All samples were below the LOQ ($< 2.5 \mu\text{g}$) for particulate CN. Per the NIOSH Method 6010, particulate cyanide results are an estimation of the actual concentration. Since the two forms of cyanide have potential to be present, both were analyzed and are reported separately in the samples analyzed by USAPHC's contract laboratory. The three consecutive training exercise samples, which consisted of a static sample point near the CBRNE NCO and sampled over a 102-401 minute duration range, were all above LOQ. The concurrent CIHL analyzed samples had a lower LOQ of $1.1 \mu\text{g}$. With the lower quantitative reporting level, the analysis results of one 15-minute duration sample out of eight 15-minute duration samples and both CBRNE NCO/supervisor exercise duration samples were found to be above the LOQ. See Appendix A for all sample results.

Table 4-1 Field Samples Above LOQ Sample Result

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (μg)	RESULTS (ppm)
082912-Full Dur.	401	74.03	4.2	0.05
090512-Full Dur.	123	24.52	2.8	0.10
090712-Full Dur.	102	20.36	3.2	0.14

Consecutive training exercise sample results

Table 4-2 Field Samples Above LOQ Sample Results

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (µg)	RESULTS (ppm)
082212-NS5	15	3.08	1.6	0.47
082212-NL1	50	10.95	2.4	0.2
082212-NL2	56	11.35	1.4	0.11

Sample results of 15-minute samples and supervisor samples, produced from CIHL analysis (NS=15 minute samples "short", NL=supervisor sample "long")

Modified Wald's Confidence Interval

The majority of sample results were below LOQ, hence creating a large set of censored data. Due to the amount of censored data, the use of the modified Wald Method for a 95% confidence interval was used. This method is used for calculating the confidence interval of proportions. Using the modified Wald Method for a 95% confidence interval (see Table 4-3), the percent of samples expected with 95% certainty to be above the 2.7 µg LOQ are 0-7.68% for 15-minute samples, 0-20.67% for supervisor samples, and 38.25-100% for samples greater than 102 minutes. At the 1.1 µg LOQ, the percent expected to be above the LOQ are 0.11-49.22% for 15-minute samples and 29.02-100% for the supervisor samples.

Table 4-3 Modified Wald Method Confidence Intervals

Sample LOQ	Sample Duration	Total Samples	Samples >LOQ	Proportion >LOQ	95% Confidence Interval
2.7 µg	15 minutes	56	0	0	0.0000-0.0768
2.7 µg	40-92 minutes	18	0	0	0.0000-0.2067
2.7 µg	>102 minutes	3	3	1	0.3825-1.0000
1.1 µg	15 minutes	8	1	0.1250	0.0011-0.4922
1.1 µg	40-92 minutes	2	2	1	0.2902-1.0000

Graphpad Software used to calculate modified Walds method 95% confidence interval

TUBE FURNACE

Overview Results

All vapor HCN NIOSH Method 6010 samples were above the LOQ of 2.7 µg. A portion of the particulate CN samples (15 of 33) were at or above the LOQ of 2.5 µg. Particulate CN results from NIOSH Method 6010 are an estimate of the mass and concentration. Results are shown in Tables 4-4 through 4-7 below and in Appendix A. Breakthrough of HCN to the back section of the sorbent tube for samples at temperatures 175-225 °C occurred. One sampling pump shut off early at the 350 °C temperature point due to battery failure.

Table 4-4 Laboratory NIOSH Method 6010 Results Vapor HCN

Temp. C°	Sample ID	Volume (L)	Time (min)	Results (µg)	Results (ppm)
100	021413-100A	94.7	470	4.5	0.043
	021413-100B	94.3	470	3.9	0.037
	021413-100C	98.4	470	5.9	0.054
125	021513-125A	95.4	470	16	0.16
	021513-125B	95.4	470	14	0.13
	021513-125C	98.8	470	15	0.14
150	021813-150A	94.4	470	6.9	0.066
	021813-150B	97.9	470	7.9	0.073
	021813-150C	96.7	470	7.7	0.072
175*	021913-175A*	94.8	470	33	0.31
	021913-175B	97.8	470	21	0.19
	021913-175C	96.9	470	29	0.27
200*	022013-200A	92.3	460	26	0.26
	022013-200B	94.2	460	33	0.32
	022013-200C*	94.2	460	38	0.37
225*	022113-225A*	91.5	450	18	0.18
	022113-225B*	94.5	450	29	0.28
	022113-225C*	91.3	450	17	0.16
250	022213-250A	91.8	450	21	0.21
	022213-250B	94.6	450	44	0.42
	022213-250C	91.1	450	38	0.37
275	021313-275A	90.6	450	51	0.51
	021313-275B	92	450	28	0.28
	021313-275C	94	450	34	0.33
300	021213-300A	85.1	420	34	0.37
	021213-300B	86.1	420	36	0.37
	021213-300C	84.8	420	40	0.43
325	020813-325A	85	420	29	0.31
	020813-325B	85.2	420	35	0.37
	020813-325C	84.7	420	30	0.32
350^	020713-350A	87.6	420	40	0.42
	020713-350B	84.5	420	38	0.41
	020713-350C	64.5	315	39	0.55

*=Breakthrough ^=one sample pump shut off early reducing sample volume by 20L

Table 4-5 Laboratory NIOSH Method 6010 Results Particulate CN

Temp. C°	Sample ID	Volume (L)	Time (min)	Results (µg)	Results (mg/m ³)
100	021413-100A	94.7	470	<2.5	<0.026
	021413-100B	94.3	470	<2.5	<0.026
	021413-100C	98.4	470	<2.5	<0.025
125	021513-125A	95.4	470	<2.5	<0.026
	021513-125B	95.4	470	<2.5	<0.026
	021513-125C	98.8	470	<2.5	<0.025
150	021813-150A	94.4	470	<2.5	<0.026
	021813-150B	97.9	470	2.6	0.027
	021813-150C	96.7	470	2.5	0.026
175*	021913-175A*	94.8	470	<2.5	<0.026
	021913-175B	97.8	470	2.5	0.026
	021913-175C	96.9	470	<2.5	<0.026
200*	022013-200A	92.3	460	<2.5	<0.027
	022013-200B	94.2	460	3.3	0.035
	022013-200C*	94.2	460	2.9	0.031
225*	022113-225A*	91.5	450	3.1	0.034
	022113-225B*	94.5	450	5.8	0.061
	022113-225C*	91.3	450	3.4	0.037
250	022213-250A	91.8	450	<2.5	<0.027
	022213-250B	94.6	450	<2.5	<0.026
	022213-250C	91.1	450	<2.5	<0.028
275	021313-275A	90.6	450	3.9	0.043
	021313-275B	92	450	<2.5	<0.027
	021313-275C	94	450	<2.5	<0.027
300	021213-300A	85.1	420	<2.5	<0.029
	021213-300B	86.1	420	<2.5	<0.029
	021213-300C	84.8	420	<2.5	<0.029
325	020813-325A	85	420	5.9	0.07
	020813-325B	85.2	420	5.2	0.061
	020813-325C	84.7	420	6.4	0.076
350^	020713-350A	87.6	420	3.2	0.036
	020713-350B	84.5	420	5	0.059
	020713-350C	64.5	315	3.7	0.057

*=Breakthrough ^=one sample pump shut off early reducing sample volume by 20L

Means and Confidence Intervals

Table 4-6 Tube Furnace Quantitative Analysis Mean and 95% Confidence Interval for Vapor HCN

Temperature °C	Mean Mass (µg)	95% CI	Mean Conc. (ppm)	95% CI
350^	39	37.87-40.13	0.46	0.37-0.55
325	31.33	27.69-34.97	0.33	0.29-0.37
300	36.67	33.21-40.13	0.39	0.35-0.43
275	37.67	24.17-51.17	0.37	0.23-0.51
250	34.33	20.83-47.83	0.33	0.21-0.45
225*	21.33	13.8-28.86	0.21	0.14-0.28
200*	32.33	28.51-39.15	0.32	0.26-0.38
175*	27.67	20.76-34.58	0.26	0.19-0.33
150	7.5	6.9-8.1	0.07	0.06-0.07
125	15	13.87-16.13	0.14	0.12-0.16
100	4.77	3.61-5.93	0.04	0.03-0.05

*=Breakthrough ^=one sample pump shut off early reducing sample volume by 20L

Table 4-7 Tube Furnace Quantitative Analysis Mean and 95% Confidence Interval for Particulate CN

Temperature °C	Mean Mass (µg)	95% CI	Mean Conc. (mg/m ³)	95% CI
350^	3.97	2.92-5.02	0.051	0.037-0.065
325	5.83	5.15-6.51	0.069	0.050-0.088
300	1.25	1.25	0.015	0.015
275	2.13	0.40-3.86	0.023	0.004-0.042
250	1.25	1.25	0.014	0.014
225*	4.1	2.43-5.77	0.044	0.027-0.061
200*	2.48	1.25-3.71	0.027	0.012-0.042
175*	1.67	0.85-2.49	0.017	0.009-0.025
150	2.12	1.27-2.97	0.022	0.012-0.032
125	1.25	1.25	0.013	0.013
100	1.25	1.25	0.013	0.013

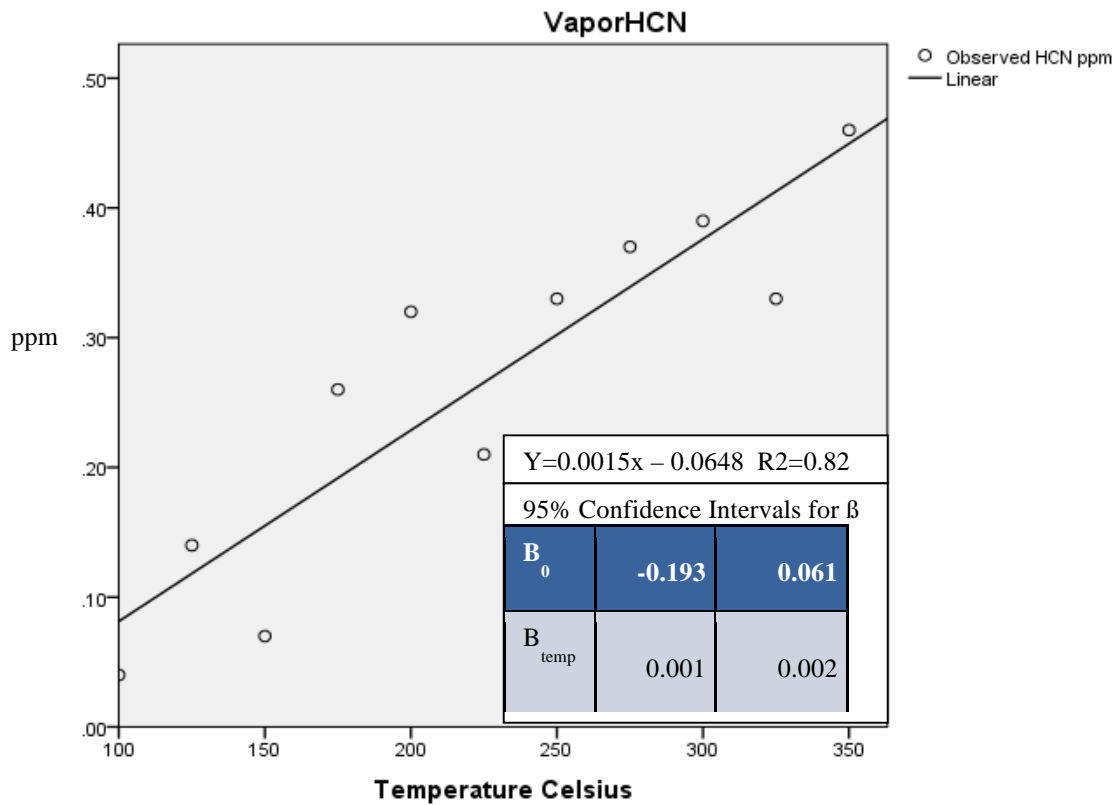
*=Breakthrough ^=one sample pump shut off early reducing sample volume by 20L; means and confidence intervals for samples below LOQ for calculated using ½ the LOQ

HCN Regression Analysis and Correlations

The concentration of vapor HCN increased linearly as the temperature of the CS dispersal increased. The coefficient of determination for this relationship (R^2) was 0.82.

The sample results used in the linear regression calculations included the sample in which the pump terminated early. The statistical test was also performed when eliminating the sample in question and results did not change significantly ($R^2 = 0.80$). The scatter plot with best fit line and equation along with β_0 and β_1 95% Confidence Interval are shown in Table 4-8.

Table 4-8 Vapor HCN Linear Regression



SPSS used for calculations

There was a significant correlation between temperature of generation and the concentration of HCN using Pearson Correlation Coefficient with an r value of 0.902 (p=0.0001).

Table 4-9 illustrates which temperatures are significantly different from each other using the Multiple Comparisons Tukey HSD. With the exception of 200 °C and 225 °C, the majority of temperatures had significant difference with those further away on the temperature range.

Table 4-9 Multiple Comparisons Tukey HSD

(I) TempC	(J) TempC	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
100C	125C	-.09867	.05293	.732	-.2879	.0905
	150C	-.02567	.05293	1.000	-.2149	.1635
	175C	-.21200*	.05293	.020	-.4012	-.0228
	200C	-.27200*	.05293	.001	-.4612	-.0828
	225C	-.16200	.05293	.139	-.3512	.0272
	250C	-.28867*	.05293	.001	-.4779	-.0995
	275C	-.32867*	.05293	.000	-.5179	-.1395
	300C	-.34533*	.05293	.000	-.5345	-.1561
	325C	-.28867*	.05293	.001	-.4779	-.0995
	350C	-.41533*	.05293	.000	-.6045	-.2261
125C	100C	.09867	.05293	.732	-.0905	.2879
	150C	.07300	.05293	.941	-.1162	.2622
	175C	-.11333	.05293	.563	-.3025	.0759
	200C	-.17333	.05293	.092	-.3625	.0159
	225C	-.06333	.05293	.976	-.2525	.1259
	250C	-.19000*	.05293	.048	-.3792	-.0008
	275C	-.23000*	.05293	.009	-.4192	-.0408
	300C	-.24667*	.05293	.004	-.4359	-.0575
	325C	-.19000*	.05293	.048	-.3792	-.0008
	350C	-.31667*	.05293	.000	-.5059	-.1275
150C	100C	.02567	.05293	1.000	-.1635	.2149
	125C	-.07300	.05293	.941	-.2622	.1162

	175C	-.18633	.05293	.056	-.3755	.0029
	200C	-.24633*	.05293	.005	-.4355	-.0571
	225C	-.13633	.05293	.317	-.3255	.0529
	250C	-.26300*	.05293	.002	-.4522	-.0738
	275C	-.30300*	.05293	.000	-.4922	-.1138
	300C	-.31967*	.05293	.000	-.5089	-.1305
	325C	-.26300*	.05293	.002	-.4522	-.0738
	350C	-.38967*	.05293	.000	-.5789	-.2005
175C	100C	.21200*	.05293	.020	.0228	.4012
	125C	.11333	.05293	.563	-.0759	.3025
	150C	.18633	.05293	.056	-.0029	.3755
	200C	-.06000	.05293	.984	-.2492	.1292
	225C	.05000	.05293	.996	-.1392	.2392
	250C	-.07667	.05293	.922	-.2659	.1125
	275C	-.11667	.05293	.524	-.3059	.0725
	300C	-.13333	.05293	.345	-.3225	.0559
	325C	-.07667	.05293	.922	-.2659	.1125
	350C	-.20333*	.05293	.028	-.3925	-.0141
200C	100C	.27200*	.05293	.001	.0828	.4612
	125C	.17333	.05293	.092	-.0159	.3625
	150C	.24633*	.05293	.005	.0571	.4355
	175C	.06000	.05293	.984	-.1292	.2492
	225C	.11000	.05293	.602	-.0792	.2992
	250C	-.01667	.05293	1.000	-.2059	.1725
	275C	-.05667	.05293	.989	-.2459	.1325
	300C	-.07333	.05293	.940	-.2625	.1159
	325C	-.01667	.05293	1.000	-.2059	.1725
	350C	-.14333	.05293	.258	-.3325	.0459
225C	100C	.16200	.05293	.139	-.0272	.3512
	125C	.06333	.05293	.976	-.1259	.2525
	150C	.13633	.05293	.317	-.0529	.3255
	175C	-.05000	.05293	.996	-.2392	.1392
	200C	-.11000	.05293	.602	-.2992	.0792
	250C	-.12667	.05293	.413	-.3159	.0625
	275C	-.16667	.05293	.118	-.3559	.0225
	300C	-.18333	.05293	.063	-.3725	.0059
	325C	-.12667	.05293	.413	-.3159	.0625
	350C	-.25333*	.05293	.003	-.4425	-.0641
250C	100C	.28867*	.05293	.001	.0995	.4779

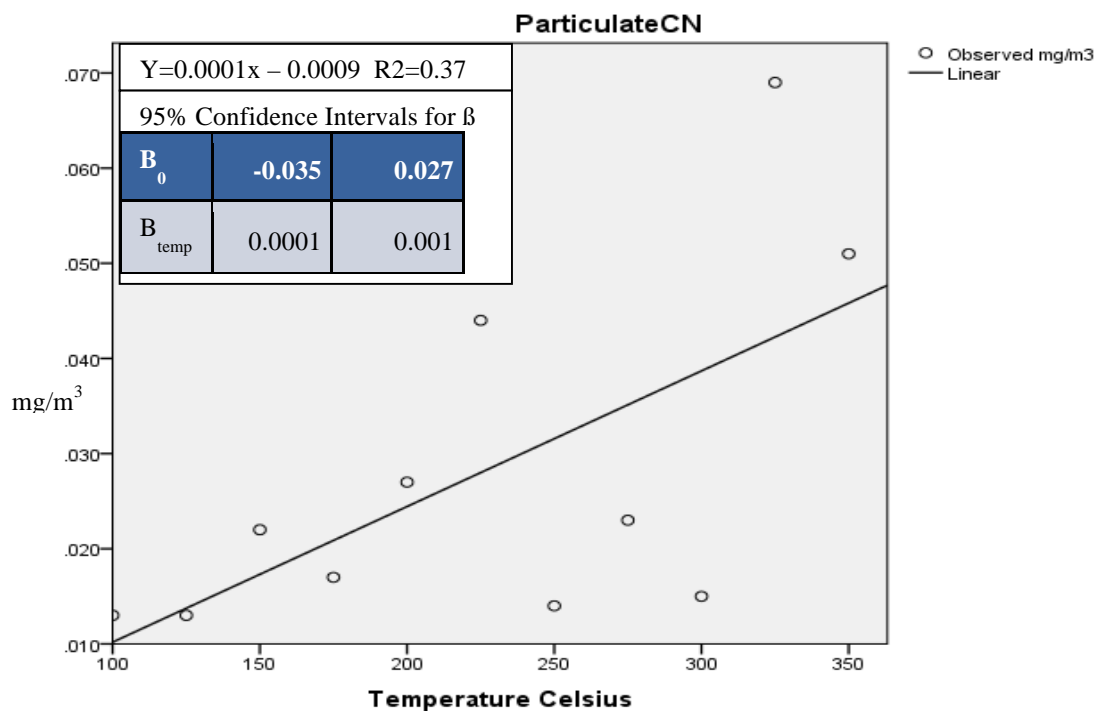
	125C	.19000*	.05293	.048	.0008	.3792
	150C	.26300*	.05293	.002	.0738	.4522
	175C	.07667	.05293	.922	-.1125	.2659
	200C	.01667	.05293	1.000	-.1725	.2059
	225C	.12667	.05293	.413	-.0625	.3159
	275C	-.04000	.05293	.999	-.2292	.1492
	300C	-.05667	.05293	.989	-.2459	.1325
	325C	.00000	.05293	1.000	-.1892	.1892
	350C	-.12667	.05293	.413	-.3159	.0625
275C	100C	.32867*	.05293	.000	.1395	.5179
	125C	.23000*	.05293	.009	.0408	.4192
	150C	.30300*	.05293	.000	.1138	.4922
	175C	.11667	.05293	.524	-.0725	.3059
	200C	.05667	.05293	.989	-.1325	.2459
	225C	.16667	.05293	.118	-.0225	.3559
	250C	.04000	.05293	.999	-.1492	.2292
	300C	-.01667	.05293	1.000	-.2059	.1725
	325C	.04000	.05293	.999	-.1492	.2292
	350C	-.08667	.05293	.850	-.2759	.1025
300C	100C	.34533*	.05293	.000	.1561	.5345
	125C	.24667*	.05293	.004	.0575	.4359
	150C	.31967*	.05293	.000	.1305	.5089
	175C	.13333	.05293	.345	-.0559	.3225
	200C	.07333	.05293	.940	-.1159	.2625
	225C	.18333	.05293	.063	-.0059	.3725
	250C	.05667	.05293	.989	-.1325	.2459
	275C	.01667	.05293	1.000	-.1725	.2059
	325C	.05667	.05293	.989	-.1325	.2459
	350C	-.07000	.05293	.954	-.2592	.1192
325C	100C	.28867*	.05293	.001	.0995	.4779
	125C	.19000*	.05293	.048	.0008	.3792
	150C	.26300*	.05293	.002	.0738	.4522
	175C	.07667	.05293	.922	-.1125	.2659
	200C	.01667	.05293	1.000	-.1725	.2059
	225C	.12667	.05293	.413	-.0625	.3159
	250C	.00000	.05293	1.000	-.1892	.1892
	275C	-.04000	.05293	.999	-.2292	.1492
	300C	-.05667	.05293	.989	-.2459	.1325
	350C	-.12667	.05293	.413	-.3159	.0625

350C	100C	.41533*	.05293	.000	.2261	.6045
	125C	.31667*	.05293	.000	.1275	.5059
	150C	.38967*	.05293	.000	.2005	.5789
	175C	.20333*	.05293	.028	.0141	.3925
	200C	.14333	.05293	.258	-.0459	.3325
	225C	.25333*	.05293	.003	.0641	.4425
	250C	.12667	.05293	.413	-.0625	.3159
	275C	.08667	.05293	.850	-.1025	.2759
	300C	.07000	.05293	.954	-.1192	.2592
	325C	.12667	.05293	.413	-.0625	.3159
* The mean difference is significant at the 0.05 level. SPSS used for calculations.						

Particulate CN Linear Regression and Correlations

Particulate CN concentration did not demonstrate a significant linear relationship with the temperature of CS dispersal. The coefficient of determination (R^2) for this relationship was 0.3662. The scatter plot with best fit line and equation along with β_0 and β_1 95% Confidence Interval are shown in Table 4-10.

Table 4-10 Particulate CN Linear Regression

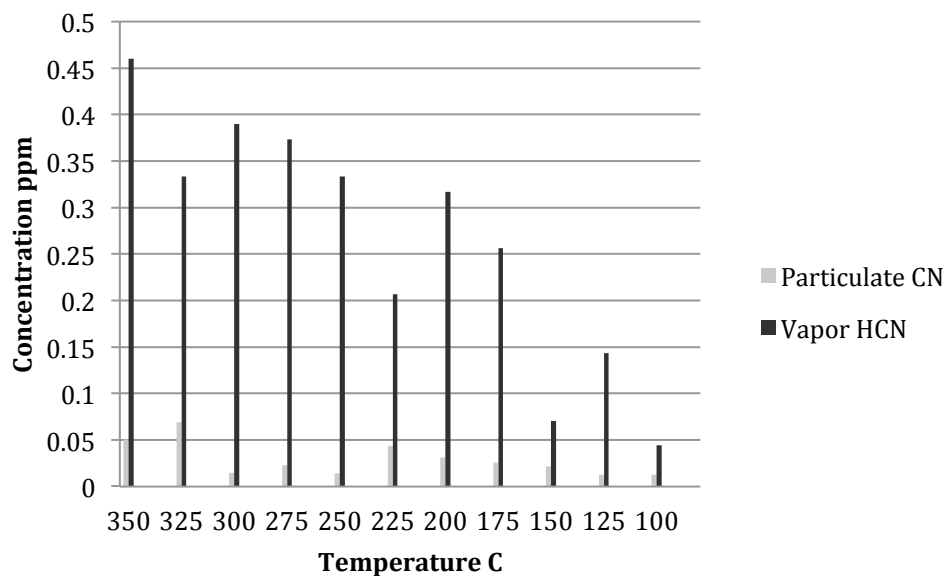


For samples below the LOQ, ½ the LOQ was used to calculate the means. SPSS used for all calculations

There was a mild correlation between temperature of generation compared to the concentration of HCN using both Pearson Correlation Coefficient ($r = 0.64$, $p = 0.036$) and Spearman's Correlation Coefficient ($r = 0.67$, $p = 0.024$). Spearman's Correlation Coefficient was used in addition to Pearson to evaluate if adjusting for the influence of outliers, assuming non- normal distribution based on R^2 , using a non-parametric ranking measure would affect the coefficient and significance. The use of the non-parametric measure improved results but did not significantly adjust the results.

Vapor HCN and Particulate CN Relationship

Table 4-11 Vapor HCN versus Particulate CN Bar Graph Comparison



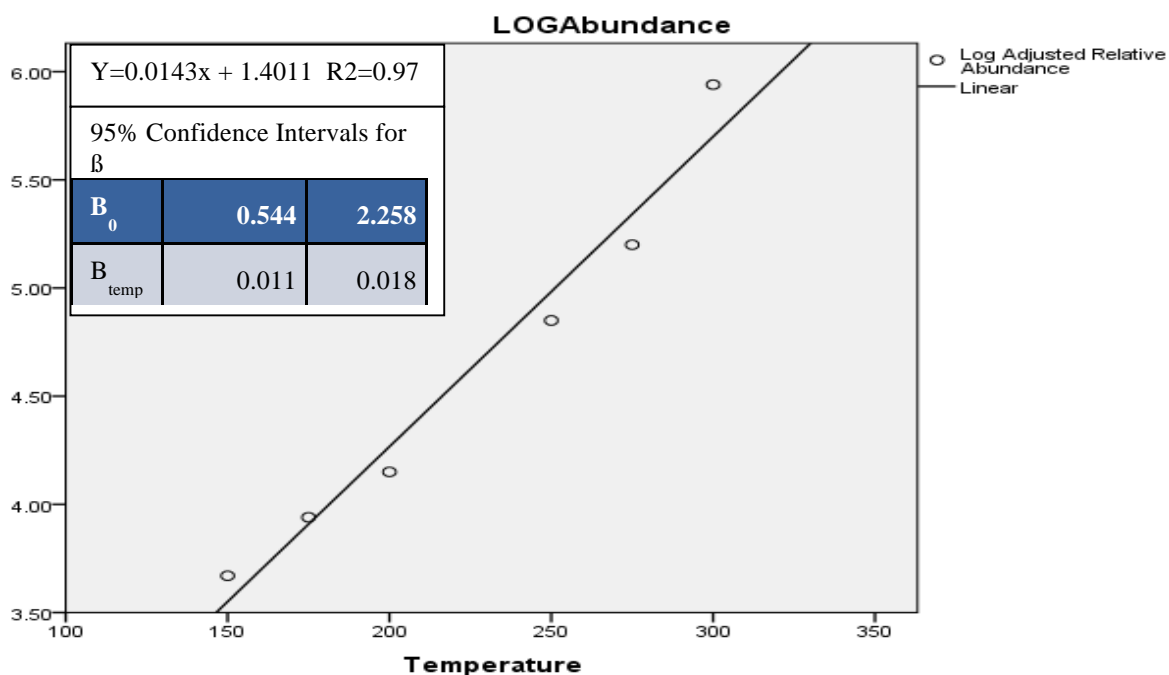
The above bar graph (Table 4-11) illustrates the relationship between the particulate CN and vapor HCN. From the graph, there appears to be no significant relationship between the particulate CN and vapor HCN (an inverse relationship was expected), but it is apparent that there was a general increase in vapor HCN concentrations as temperatures rose. There was also no significant correlation between the concentration of vapor HCN and particulate CN concentration with Pearson Correlation Coefficient ($r = 0.38$, $p = 0.25$) or Spearman's Correlation Coefficient ($r = 0.45$, $p = 0.17$). Spearman's Correlation Coefficient was used in addition to Pearson to evaluate whether or not adjusting for outliers using a non-parametric ranking measure

would affect the coefficient and significance. The use of the non-parametric measure, while increasing the correlation and significance, did not significantly adjust the results

Qualitative Linear Regression and Correlations

Linear regression calculations with Pearson correlation coefficient were calculated for the results of the preliminary study conducted by Hout *et al.* (Tables 4-12) to compare the results obtained with SPME to the results obtained through NIOSH Method 6010. The relative abundance results were log-adjusted to account for the magnitude of results (10^3 to 10^6). The significance of the difference between the correlation coefficients of vapor HCN quantification ($r=0.902$ and $n=11$), and the SPME log adjusted relative abundance ($r=0.983$ and $n=6$), was calculated using vasarstats.net. A two tailed p value of 0.1868 was obtained indicating the difference was not significant.(34)

Table 4-12SPME Log Adjusted Linear Regression



CHAPTER 5: Discussion

CHAMBER SAMPLING

Standards Comparisons

Results from sampling were compared to established occupational exposure guidelines from numerous federal agencies. The comparative guidelines included the USAPHC 10-minute and 1-hour MEGs, the EPA 10-minute, 30-minute, 1-hour, and 4-hour AEGLs, the NIOSH-REL-STEL, and the ACGIH Ceiling Limit. The EPA AEGLs were developed to reflect acute exposure to the general population to include susceptible persons.(40) The USAPHC MEG for HCN are based on the EPA's AEGLs.(39) Both the AEGLs and MEGs are based on the whole body effects, primarily to the CNS, lungs, and thyroid.(28; 39) These standards were chosen for comparison instead of the OSHA Permissible Exposure Level (PEL) due to the MEGs accommodating for susceptible subpopulations within the military population such as asthmatics.(39) The tables below show MEG and AEGL limits (Tables 5-1 and 5-2).

Table 5-1 Military Exposure Guidelines

HCN MEG (ppm)	10 minutes	1 hour	8 hours
Negligible	2.5	2.0	1.0
Marginal	17	7.1	---
Critical	27	15	---

Comparison of HCN concentrations were made to the 10-minute and 1-hour MEGs

Table 5-2 Acute Exposure Guideline Levels

HCN AEGL (ppm)	10 minutes	30 minutes	60 minutes	4 hours	8 hours
AEGL 1	2.5	2.5	2.0	1.3	1.0
AEGL 2	17	10	7.1	3.5	2.5
AEGL 3	27	21	15	8.6	6.6

Comparison of HCN concentrations were made to the 10-minute, 30-minute, 60-minute, and 4-hour AEGLs

Negligible and AEGL 1 are defined as an exposure that could cause notable discomfort, irritation, or asymptomatic non-sensory effects. These effects are not disabling, are transient, and upon cessation of exposure are reversible. Marginal and AEGL 2 are defined as an exposure that could cause irreversible or other serious long lasting effects or impair escape ability. Critical and AEGL 3 are defined as an exposure that could cause life threatening effects or death.(39; 40)

The Occupational exposure guidelines used for comparisons to the study results (STEL and ceiling limits) were developed based on a healthy worker population; sensitive populations and those with chronic medical conditions were excluded in development of standards. Both STEL and ceiling limits are used for acute exposure effects of chemicals. The NIOSH REL-STEL is 4.7 ppm, and the ACGIH has a ceiling limit of 4.7 ppm. Both guidelines have a skin notation indicating skin, mucous membrane, and eye routes represent potentially significant exposure. ACGIH based the ceiling limit on acute poisoning risk while NIOSH based its REL-STEL on thyroid, blood, and respiratory effects.(30)

Table 5-3 Result Comparison

Sample	TIME (Min)	Result (ppm)	Mean Results (ppm)	60-min AEGL/1-hour MEG (ppm)	4-hour AEGL (ppm)	8-hour AEGL/MEG (ppm)
082912-Full Dur.	401	0.05	0.1	N/A	1.3-8.6	1-6.6
090512-Full Dur.	123	0.10		2-15	1.3-8.6	N/A
090712-Full Dur.	102	0.14		2-15	1.3-8.6	N/A

Comparison of consecutive training exercise sample results to guidelines.

Table 5-4 Result Comparison

Sample	Time (Min)	Result (ppm)	Mean Results (ppm)	STEL/Ceiling (ppm)	10-min AEGL/MEG (ppm)	30-min AEGL (ppm)	60-min AEGL/1-hour MEG (ppm)
082212-NS5	15	0.47	0.47	4.7	2.5-27	2.5-21	N/A
082212-NL1	50	0.2	0.16	N/A	N/A	2.5-21	2-15
082212-NL2	56	0.11		N/A	N/A	2.5-21	2-15

Comparison CIHL analyzed results to guidelines.

Concentrations of HCN at 200 °C in a field setting at Ft. Jackson during live training exercises, were detectable and quantifiable provided sufficient sample volume of contaminated air was sampled. This temperature level was much lower than the previously determined threshold of generation of HCN, 275 °C hypothesized and 350 °C quantified. This is not only interesting academically, but demonstrates potential exposures that were previously thought not to be present. However, the airborne HCN levels detected were well below the established exposure guidelines (Tables 5-3 and 5-4).

While these concentrations are below the levels that could cause significant acute health problems in humans, it is still worthwhile to note that there may be potential chronic effects from long-term exposures to low levels of HCN if adequate personnel protective equipment is not utilized. Previous studies have indicated potential effects from low levels of HCN on a chronic basis at levels near those detected at Ft. Jackson.(11; 13) This is an important consideration for Soldiers who work in occupational specialties that have higher exposure frequencies than the average Soldier (such as a CBRNE NCO who works at a basic training confidence chamber may be in a CS environment up to 5 times a week or more). Though inhalation is a primary concern with HCN, dermal absorption also contributes to the overall exposure/dose and as with the case of CS, heat/humidity increases the absorption of HCN.(8) While those Soldiers who work with CS and/or in a CS atmosphere on a regular basis normally wear the M40 air purifying mask, the use of dermal protection is not as consistent as demonstrated in Figures 3-1 and 3-10 through 3-12.

Comparison to Past Research

In comparison to past field sampling at higher temperatures, results from this study were below the concentrations that were recorded for the Kluchinsky *et al.* research (significantly higher temperature at >700 °C) but closer to the concentrations of airborne HCN that were obtained by an Air Force IH survey. Table 5-5 illustrates the comparisons.(12; 20) Of importance to note, the quantity of the CS employed during the Air Force industrial hygiene survey was significantly less than the amount of CS that was employed during the Ft. Jackson, SC field sampling [~4 capsules (~2.4 g) compared to 34-68 capsules (~20.4 – 40.8 g)].(12)

Table 5-5 Comparison to Previous HCN Quantification Studies Using NIOSH Methods in the Collection and Analysis of Field Samples

Study	Method	Temperature	Volume Collected (L)	Concentration (ppm)
Army IH Survey 2001	7904	Unknown, estimated >1000 °C	unknown	<0.009
Kluchinsky(20) 2002	7904	>700 °C	14.94-15.98	3.9-5.4
Kluchinsky(20) 2002	6010	>700 °C	1.66-1.68	10-15
Air Force IH Survey(12) 2011	6010	350-700 °C	unknown	0.14-0.18
Kanapathy (samples above LOQ)	6010	200 °C	3.08-74.03	0.05-0.47

Limitations

The field sampling study had several limitations to note. The first limitation was that this study was an observational study. While an observational study has many advantages, there are also limitations; control over amount of CS combusted, length of combustion, whether or not consecutive exercises occurred, and duration that the supervisor is the chamber lies with the personnel conducting the exercise and not the researcher. This may affect the concentrations of HCN detected and individual exposure times. With the large percentage of censored data (samples below the LOQ), the route of statistical analysis was modified to approach the results as a proportion instead of an estimation of a mean. Post hoc, this created a need for an increased number of samples to obtain a narrower range of the predicted proportion above LOQ that could be obtained. In addition the volume of air sampled needs to be increased to detect at the 2.7 µg limit of quantification, primarily through an increase in flow rate and not increase in exposure

duration due to the study being observational in nature. In addition, more sampling during consecutive exercises and sample analysis through a laboratory with lower LOQ for 15 minute duration samples and supervisor samples needs to be conducted. It is important to remember, while the samples may fall below LOQ, it does not necessarily mean that the substance is not present, which was shown with three samples falling in between the two different LOQs (1.1 and 2.7 μg).

TUBE FURNACE

Observations

Several notable observations were made during the thermal degradation of CS within the tube furnace reaction system which raises additional questions regarding the combustion (endothermic degradation) processes of CS at these lower temperatures. The following was visually observed during the tube furnace experiment:

1. Visible white exhaust was present 250-350 °C. Exhaust was not visible below 250 °C. At 250-350 °C fine particles were noted. A large quantity of crystal-like fibers from 100-225 °C were present. These fibers were approximately between 0.2-1 cm in length. This created occasional blockage of the sorbent tubes. This may have affected results, in particular particulate CN. This may be from incomplete combustion below 250 °C.
2. Soda lime sorbent tubes turned from white to purple completely through, front to back of sorbent tube, from 100-225 °C. Soda lime is manufactured with an indicator dye that turns purple when exposed to carbon dioxide in concentrations that exhaust the absorptive capacity and thus cause breakthrough (loss) of the analyte of interest.(1) While it is possible that CO_2 was the cause of this observation, another chemical may have caused the

interference. This may have affected results by hindering the ability of sorbent to capture the HCN and subsequent loss of some of the HCN analyte. At 250-275 °C there was a minimal band of purple discoloration at the front end of the sorbent. At 300-350 °C, no purple discoloration was noted. This finding warrants further investigation to determine whether or not CO₂ was the source.

Quantification

Quantification of HCN was obtained at all temperatures sampled (100-350 °C) for vapor HCN in a linear relationship; concentration of HCN increased as temperature of generation increased. Particulate CN was present at various temperatures but did not present in a linear relationship to temperature. Results that were less than the LOQ (2.5 µg) for particulate CN were assessed statistically using ½ the LOQ (1.25 µg). The use of ½ the LOQ for the concentration of samples that presented below the LOQ may create either an over or underestimation of the amount of particulate CN generated. Obtaining particulate CN in the laboratory sampling and not the field sampling may have been aided by the proximity of the collection devices (sorbent tubes and/or SPME) to the point of generation and the flow gas but inhibited by periodic particulate blockage of sorbent tubes at temperatures 100-225 °C. The concentration of particulate CN generated was compared to the concentration of vapor HCN generated. No linear or significant relationship was determined (an inverse relationship was anticipated, the greater concentration of vapor HCN the reduced concentration of particulate CN due to combustion processes), nor did adding the particulate CN results to the vapor HCN results adjust the best fit line significantly. The mean concentrations at each temperature

point are listed in Tables 5-6 (vapor HCN) and 5-7 (particulate CN). HCN was detected at a much lower temperature than had previously been demonstrated or hypothesized in past research, though a threshold of generation was not determined. Of note, when compared to established exposure guidelines, all concentrations were well below the exposure guidelines.

Table 5-6 Tube Furnace Quantitative Analysis Mean Concentration and 95% Confidence Interval for Vapor HCN

Temperature °C	Mean Conc. (ppm)	95% CI	ACGIH Ceiling	8 hour EPA AEGL-1 and USAPHC MEG- Negligible
350^	0.46	0.37-0.55	4.7	1.0
325	0.33	0.29-0.37		
300	0.39	0.35-0.43		
275	0.37	0.23-0.51		
250	0.33	0.21-0.45		
225*	0.21	0.14-0.28		
200*	0.32	0.26-0.38		
175*	0.26	0.19-0.33		
150	0.07	0.06-0.07		
125	0.14	0.12-0.16		
100	0.04	0.03-0.05		

*=Breakthrough ^=one sample pump shut off early reducing sample volume by 20L

Table 5-7 Tube Furnace Quantitative Analysis Mean and 95% Confidence Interval for Particulate CN

Temperature °C	Mean Conc. (mg/m ³)	95% CI
350 [^]	0.051	0.037-0.065
325	0.069	0.050-0.088
300	0.015	0.015
275	0.023	0.004-0.042
250	0.014	0.014
225*	0.044	0.027-0.061
200*	0.027	0.012-0.042
175*	0.017	0.009-0.025
150	0.022	0.012-0.032
125	0.013	0.013
100	0.013	0.013

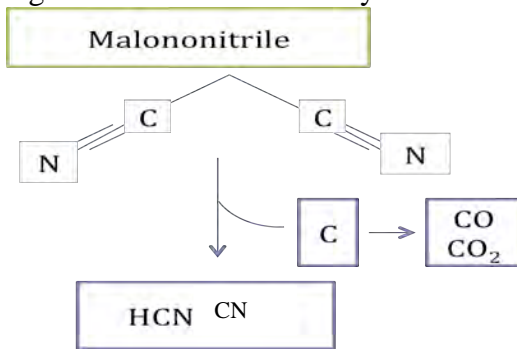
*=Breakthrough [^]=one sample pump shut off early reducing sample volume by 20L ()=one sample above LOQ; ½ LOQ used for samples below LOQ

HCN Generation from Malononitrile

The presence of HCN at temperatures as low as 100 °C necessitates discussion on the plausible generation of HCN at such relatively low temperatures of thermal CS degradation. Malononitrile was demonstrated in previous research as being present at 150 °C, the lowest temperature investigated, and it contains two cyanide molecules.(16) Malononitrile may be present at or below 100 °C and may be the primary source of HCN as a thermal degradation by-product at low temperatures of CS dispersal (Figure 5-1). Malononitrile has a melting point of 32 °C (indicative of less energy needed to decompose than CS) and boiling point of 220 °C. (25) This presents the hypothesis of degradation from malononitrile at temperatures lower than that evaluated for CS, if malononitrile is emitted from CS below 100 °C. Compounds such as malononitrile and CS that contain nitrogen and carbon, under thermal conditions, will create the loss of cyanide molecule.(29) Further investigation into the malononitrile compound is needed to further the knowledge of CS thermal breakdown processes and the malononitrile

compound itself. As CS is known to be thermally unstable, further research into the threshold of CS stability could further the understanding of the chemical.(26)

Figure 5-1 Potential Pathway HCN Genetration from Malononitrile

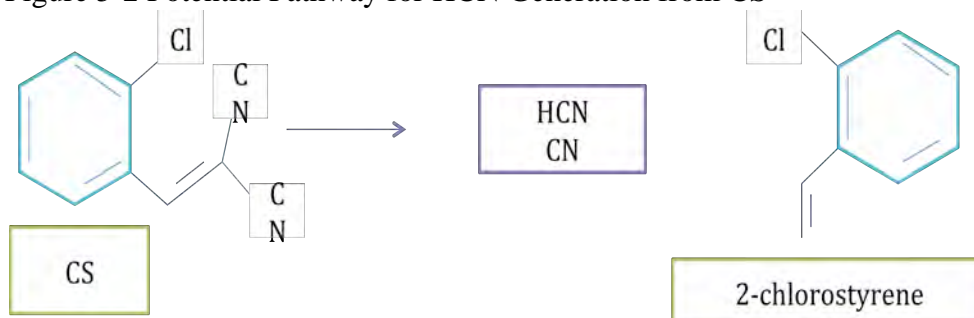


Alternate Pathways of HCN Generation

While generation of HCN from malononitrile seems to be the most probable route of generation at the low end of the temperature range that has been investigated (100-300 °C), there are multiple different ways that HCN could be generated from CS. One pathway that has not been mentioned in previous research is the degradation by-product 2-chlorostyrene (Figure 5-2). In research conducted by Hout *et al.*, 2-chlorostyrene was found qualitatively by the use of SPME at 175 °C.(16) The loss of two cyanide molecules from the CS compound through thermal decomposition would leave the compound 2-chlorostyrene (Figure 5-2). It may be possible that this compound is present below the previously determined temperature of 175 °C. Several other of the compounds that contain cyanide molecules (including benzonitrile at 300 °C, 2 chlorobenzonitrile at 225 °C , benzylidene malononitrile at 225 °C , and 2-chlorohydrocinnamonnitrile at 225 °C) were demonstrated to occur at higher temperatures than 175 °C.(16) With HCN appearing as low as 100 °C and increasing in concentration as the temperature of CS

degradation increases, this may be indicative of recombination and further degradation of the compounds that contain the cyanide molecules.

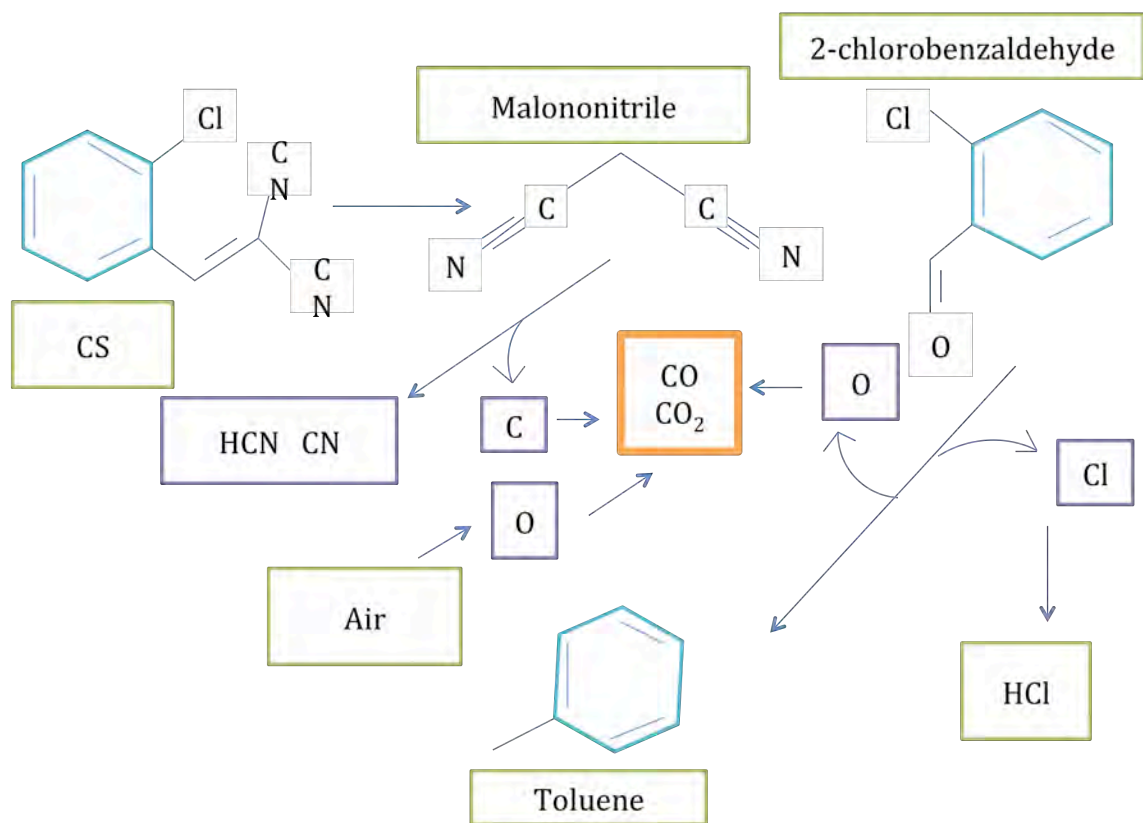
Figure 5-2 Potential Pathway for HCN Generation from CS



Carbon Dioxide Generation

Visual observations made during the tube furnace experiment indicate the possible presence of CO_2 in potentially significant quantities at 100-225 °C. Previous research has shown CO_2 generation at temperatures of CS degradation that are greater than 600 °C.(31) Figure 5-3 shows a potential route of CO_2 generation within the lower temperature range of CS thermal degradation.

Figure 5-3 Possible Mechanism for Release of CO₂



Comparison Quantitative to Preliminary Qualitative Data

Table 5-8 Quantitative Data Compared to Qualitative Data

Temperature °C	Mean Relative Abundance SPME	Mean Concentration HCN NIOSH Method 6010 (ppm)
350	N/A	0.46
325	N/A	0.33
300	8.7 x 10 ⁵	0.39
275	1.6 x 10 ⁵	0.37
250	7.1 x 10 ⁴	0.33
225	N/A	0.21
200	1.6 x 10 ⁴	0.32
175	8.8 x 10 ³	0.26
150	4.7 x 10 ³	0.07

Preliminary data include 150-300 °C; 100-125 °C CAR/PDMS SPME with GC/NPD analysis; 150-300 °C CW/DVD SPME with GC/MS analysis.

The preliminary study's qualitative analysis results (Table 5-8) showed a linear relationship between the relative abundance and temperature of CS aerosolization with an increase in strength when log adjusted. When log adjusted, the linear relationship was stronger than compared to quantification using NIOSH Method 6010. Even with an increased coefficient of determination, a comparison of the Pearson correlation coefficients demonstrated no significant difference between the two correlations (SPME and NIOSH Method 6010). These results demonstrated that SPME sampling may have potential for the utilization in detecting and estimating short exposure concentrations (i.e. the ~ 1-2 minutes that Soldiers have their masks off) when determining CS combustion protocols. The limitations of using SPME may prevent this method from being regularly used to determine HCN concentrations during live training. These limitations are based on the rapid availability of a GC with detector and calibration methods (field or laboratory based). These resource limitations may lead to limiting the use of SPME to assist in determining protocol for the quantity of CS that is combusted and the temperature range in which CS dispersed. If equipment is available for the use of SPME with appropriate analysis in a field setting, this technique could prove to be useful in providing "real time" airborne concentration estimates for short exposure durations and evaluating exposure complaints.

Limitations

The greater LOQ (2.7 μ g versus 1.1 μ g) required the use of multiple capsules and the maximum volume air to be sampled to ensure enough HCN was captured to quantify. Possible carbon dioxide (demonstrated by the soda lime sorbent color change from white to purple) generated within the reaction tube at 100-225 °C posed a breakthrough issue at 175-225 °C by exhausting the absorptive capability of the soda lime sorbent and may

have created an underestimation of HCN quantity. The apparent presence of carbon dioxide in a larger percentage at temperatures less than 250 °C warrant further investigation. Large crystal fibers formed at 100-225 °C, creating occasional blockage at the sorbent tube entrance. This may have affected the quantity of particulate CN, and to a lesser extent vapor HCN, leading to underestimating amount generated.

CHAPTER 6: Conclusion and Future Research

CONCLUSION

This research advances the understanding of military occupational exposures as it relates to the use of CS during Chemical, Biological, Radiological, Nuclear, and Explosive (CBRNE) training, an aspect of military life that affects all Soldiers from basic training (enlisted and officer) to annual training and deployment training. When combusting CS at 200 °C, within a live training CS chamber, concentrations of HCN were well below the established exposure guidelines. The 200 °C temperature point was the lowest temperature in which sampling for HCN has been conducted in a field setting and during live training exercises.(12; 15; 16; 20; 37; 41) When sampling for HCN within the temperature range of 100-350 °C, in a laboratory setting, a linear relationship between the temperature of CS dispersal and quantity of HCN was obtained, using NIOSH Method 6010. In the laboratory, HCN was generated over a range of CS thermal degradation temperatures that previously had been considered too low to produce HCN. The presence of HCN as a thermal degradation by-product at 100 °C was demonstrated; a generation point that is significantly lower than previous research has shown.

Findings suggest that low CS combustion temperatures (<200 °C) may not produce acutely hazardous airborne HCN concentrations within mask confidence chambers similar in structure and design as the chamber in Ft. Jackson, when operated under similar environmental conditions and when using similar capsule delivery methods. The study also suggests that under similar conditions to this study, DoD doctrine policies related to CS combustion procedures may be more protective of health if they do not exceed these temperature settings. While concentrations of HCN obtained were well

below the established exposure guidelines, further investigation into chronic exposure effects at these levels is warranted given that a subset of Soldiers are exposed on a more frequent occupational basis.

POTENTIAL FUTURE RESEARCH

Qualitative and Quantitative Analysis of HCN at Generation Temperatures Below the Melting Point of CS

HCN was quantitatively determined to be present at 100 °C, 5 °C above the melting point of CS. With HCN present at such a low temperature of CS dispersal, it may be possible that HCN is emitted at temperatures below the melting point of CS. Qualitative analysis followed by quantitative analysis of HCN at CS combustion temperatures below 95 °C (melting point of CS) to further characterize the threshold for generation may be warranted (CS storage related issue).

Differences in CS Degradation at ≤ 225 °C versus ≥ 250 °C

Observations during the tube furnace experiment showed a marked difference in the visual exhaust of the aerosolized CS and potential by-products between 225 °C and 250 °C. This point demonstrated a change in particle size, visible versus non-visible exhaust, and complete exhaustion of soda lime sorbent at 225 °C compared to minimal exhaustion at 250 °C. These observations create questions as to what is happening at these temperatures and why these temperature points are significant to these visual observations.

Direct Measurement of HCN in Tube Furnace

At the 350 °C temperature point, one of the three samples was terminated early due to battery failure in the pump. Even with the reduced volume of sample, the amount of HCN obtained fell in between the other two samples. This result leads to the questions as to when does HCN begin generation during CS combustion, when does generation peak, and when does HCN generation cease or become minimized. The use of a direct

reading instrument in a laboratory setting may assist in solving these questions about the behavior of HCN as it relates to generation from thermal dispersal of CS.

Field Sampling <200 °C

Qualitative and quantitative field sampling at lower temperatures is warranted with the determination of the presence of HCN <200 °C in a laboratory setting. Field sampling in an environmental chamber or RCA training chamber may help combat soda lime sorbent exhaustion and sorbent tube clogging issues encountered during the tube furnace experiment at the 100-225 °C range of CS thermal dispersion. The air atmosphere would more accurately reflect exposure potential and behavior of by-product generation during training situations. A maximum volume of air sampled and adequate quantity of CS burned would need to occur to ensure detection.

Quantification with SPME/Comparison to NIOSH Method Results

Further investigation is warranted into determining whether or not use of SPME for quantification of HCN in a CS atmosphere is comparable to the NIOSH and OSHA Methods of quantification for HCN (NIOSH 6010, NIOSH 7904, OSHA 1015).

Other Methods of Quantification

The risk of inhalation exposure to CS and HCN generally occurs in an estimated one minute timeframe. The use of sampling techniques, such as needle trap, may be warranted for investigation as to whether or not the techniques can reliably sample for one minute in a CS atmosphere. A one minute sample can give a better picture of the inhalation exposure hazard.

Biomarkers of exposure

The ultimate measurement of exposure that individual receives and uptakes into their system would be to analyze biomarkers. Both CS and HCN have dermal absorption

capabilities, the use of biomarkers (such as thiocyanate in urine) can give a more complete picture to the overall body burden from exposure.

Quantification of Malononitrile

Malononitrile is a primary breakdown product of CS through hydrolysis. At 150 °C, malononitrile has been demonstrated to form as a degradation by-product from thermal aerosolization of CS. With the presence of HCN at 100 °C, malononitrile may have a lower threshold of generation. Quantification and qualitative analysis of malononitrile below 150 °C to a point below CS melting point would give greater insight into the degradation of CS. Malononitrile is noted to have a greater toxicity than CS with its toxicity similar to cyanides. This compound also has both skin and eye irritant capability, similar to CS.(19) Quantification of malononitrile during live chamber training exercises with comparisons to CS concentrations would represent interesting aspect of CBRNE training to look at with the similarities of irritant capability.

Carbon Dioxide Generation at CS Dispersal Temperature Range 100-250 °C

A significant observation during the tube furnace experiment was the change in color of the soda lime sorbent completely turning from white to purple at 100-225 °C with minimal purple coloration at 250-275 °C. During the field sampling (200 °C) several of the longer duration samples had minimal purple coloration. Soda lime will turn purple when the absorption capability has been exhausted by carbon dioxide. Investigation into the potential presence of a large percentage of carbon dioxide at the lower combustion temperatures may be warranted, as this compound may be interfering with quantification and accurate characterization of HCN.

APPENDIX A

FIELD SAMPLE RESULTS

Table A-1: Field NIOSH Method 6010 15 minute sample results

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (µg)	RESULTS (ppm)
081512-1S	15	3.07	<2.6	<0.77
081512-2S	15	3.07	<2.6	<0.77
081512-3S	15	3.07	<2.6	<0.77
081512-4S	15	3.07	<2.6	<0.77
081612-1S	15	3.02	<2.6	<0.79
081612-2S	15	3.02	<2.6	<0.79
081612-3S	15	3.02	<2.6	<0.79
081612-4S	15	3.02	<2.6	<0.79
081712-1S	15	3.04	<2.6	<0.77
081712-2S	15	3.04	<2.6	<0.77
081712-3S	15	3.04	<2.6	<0.77
081712-4S	15	3.04	<2.6	<0.77
081812-1S	15	3.06	<2.6	<0.77
081812-2S	15	3.06	<2.6	<0.77
081812-3S	15	3.06	<2.6	<0.77
081812-4S	15	3.06	<2.6	<0.77
082012-1S	15	3.04	<2.6	<0.77
082012-2S	15	3.04	<2.6	<0.77
082012-3S	15	3.04	<2.6	<0.77
082012-4S	15	3.04	<2.6	<0.77
082112-1S	15	3.03	<2.6	<0.78
082112-2S	15	3.03	<2.6	<0.78
082112-3S	15	3.03	<2.6	<0.78
082112-4S	15	3.03	<2.6	<0.78
082212-1S	15	2.87	<2.6	<0.82
082212-2S	15	2.87	<2.6	<0.82
082212-3S	15	2.87	<2.6	<0.82
082212-4S	15	2.87	<2.6	<0.82
082212-5S	15	2.87	<2.6	<0.82
082212-6S	15	2.87	<2.6	<0.82
082212-7S	15	2.87	<2.6	<0.82
082212-8S	15	2.87	<2.6	<0.82
082412-1S	15	3.02	<2.6	<0.79
082412-2S	15	3.02	<2.6	<0.79
082412-3S	15	3.02	<2.6	<0.79
082412-4S	15	3.02	<2.6	<0.79
082712-1S	15	2.99	<2.6	<0.79
082712-2S	15	2.99	<2.6	<0.79

082712-3S	15	2.99	<2.6	<0.79
082712-4S	15	2.99	<2.6	<0.79
082912-1SA	15	2.74	<2.6	<0.86
082912-2SA	15	2.74	<2.6	<0.86
082912-3SA	15	2.74	<2.6	<0.86
082912-4SA	15	2.74	<2.6	<0.86
082912-1SB	15	2.74	<2.6	<0.86
082912-2SB	15	2.74	<2.6	<0.86
082912-3SB	15	2.74	<2.6	<0.86
082912-4SB	15	2.74	<2.6	<0.86
090512-1S	15	2.94	<2.6	<0.80
090512-2S	15	2.94	<2.6	<0.80
090512-3S	15	2.94	<2.6	<0.80
090512-4S	15	2.94	<2.6	<0.80
090512-5S	15	2.94	<2.6	<0.80
090512-6S	15	2.94	<2.6	<0.80
090512-7S	15	2.94	<2.6	<0.80
090512-8S	15	2.94	<2.6	<0.80

S=15 minute sample; All Particulate cyanide samples <2.5 µg (LOQ).

Table A-2: Field NIOSH Method 6010 Blanks

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (µg)	RESULTS (ppm)
082912-Blank	NA	NA	<2.6	-----
083012-Blank	NA	NA	<2.6	-----
082212-Blank	NA	NA	<2.6	-----
082112-Blank	NA	NA	<2.6	-----
081812-Blank	NA	Na	<2.6	-----
081612-Blank	NA	NA	<2.6	-----
090512-Blank	NA	NA	<2.6	-----
Media Blank	NA	NA	<2.6	-----
Media Blank	NA	NA	<2.6	-----

All Particulate cyanide samples <2.5 µg (LOQ).

Table A-3: Field NIOSH Method 6010 CBRNE NCO samples

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (µg)	RESULTS (ppm)
081512-1L	81	16.97	<2.6	<0.14
081612-1L	82	16.74	<2.6	<0.14
081712-1L	92	18.5	<2.6	<0.13
081812-1L	54	10.84	<2.6	<0.22
082012-1L	94	18.81	<2.6	<0.13
082112-1L	89	18.26	<2.6	<0.13
082212-1L	61	11.91	<2.6	<0.20
082212-2L	57	11.13	<2.6	<0.21

082412-1L	65	13.09	<2.6	<0.18
082712-1L	46	9.28	<2.6	<0.25
082912-1LA	58	10.37	<2.6	<0.23
082912-1LB	51	9.12	<2.6	<0.26
090512-1L	47	9.42	<2.6	<0.25
090512-2L	51	10.22	<2.6	<0.23
090712-1L	40	8.26	<2.6	<0.28
090712-2L	42	8.68	<2.6	<0.27

All Particulate cyanide samples <2.5 µg (LOQ).

Table A-4: Field NIOSH Method 6010 Consecutive Companies Samples

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (µg)	RESULTS (ppm)
082912-Full Dur.	401	74.03	4.2	0.05
090512-Full Dur.	123	24.52	2.8	0.10
090712-Full Dur.	102	20.36	3.2	0.14

All Particulate cyanide samples <2.5 µg (LOQ).

Table A-5: Field NIOSH Method 6010 CIHL Samples

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (µg)	RESULTS (ppm)
082212-NS1	15	3.08	<1.1	<0.32
082212-NS2	15	3.08	<1.1	<0.32
082212-NS3	15	3.08	<1.1	<0.32
082212-NS4	15	3.08	<1.1	<0.32
082212-NS5	15	3.08	1.6	0.47
082212-NS6	15	3.08	<1.1	<0.32
082212-NS7	15	3.08	<1.1	<0.32
082212-NS8	15	3.08	<1.1	<0.32
082212-NL1	50	10.95	2.4	0.2
082212-NL2	56	11.35	1.4	0.11
082212-NB1	BLANK	NA	<1.1	-----
082212-NB2	BLANK	NA	<1.1	-----

Highlighted samples above LOQ; Particulate cyanide not analyzed.

TUBE FURNACE SAMPLE RESULTS

Table A-6 Laboratory NIOSH Method 6010 Results Vapor HCN

Temp. C°	Sample ID	Volume (L)	Time (min)	Results (µg)	Results (ppm)
100	021413-100A	94.7	470	4.5	0.043
	021413-100B	94.3	470	3.9	0.037
	021413-100C	98.4	470	5.9	0.054
125	021513-125A	95.4	470	16	0.16
	021513-125B	95.4	470	14	0.13
	021513-125C	98.8	470	15	0.14
150	021813-150A	94.4	470	6.9	0.066
	021813-150B	97.9	470	7.9	0.073
	021813-150C	96.7	470	7.7	0.072
175	021913-175A	94.8	470	33	0.31
	021913-175B	97.8	470	21	0.19
	021913-175C	96.9	470	29	0.27
200	022013-200A	92.3	460	26	0.26
	022013-200B	94.2	460	33	0.32
	022013-200C	94.2	460	38	0.37
225*	022113-225A	91.5	450	18	0.18
	022113-225B	94.5	450	29	0.28
	022113-225C	91.3	450	17	0.16
250	022213-250A	91.8	450	21	0.21
	022213-250B	94.6	450	44	0.42
	022213-250C	91.1	450	38	0.37
275	021313-275A	90.6	450	51	0.51
	021313-275B	92	450	28	0.28
	021313-275C	94	450	34	0.33
300	021213-300A	85.1	420	34	0.37
	021213-300B	86.1	420	36	0.37
	021213-300C	84.8	420	40	0.43
325	020813-325A	85	420	29	0.31
	020813-325B	85.2	420	35	0.37
	020813-325C	84.7	420	30	0.32
350^	020713-350A	87.6	420	40	0.42
	020713-350B	84.5	420	38	0.41
	020713-350C	64.5	315	39	0.55

*=Breakthrough ^=One sample terminated early

Table A-7 Laboratory NIOSH Method 6010 Results Particulate CN

Temp. C°	Sample ID	Volume (L)	Time (min)	Results (µg)	Results (mg/m ³)
100	021413-100A	94.7	470	<2.5	<0.026
	021413-100B	94.3	470	<2.5	<0.026
	021413-100C	98.4	470	<2.5	<0.025

125	021513-125A	95.4	470	<2.5	<0.026
	021513-125B	95.4	470	<2.5	<0.026
	021513-125C	98.8	470	<2.5	<0.025
150	021813-150A	94.4	470	<2.5	<0.026
	021813-150B	97.9	470	2.6	0.027
	021813-150C	96.7	470	2.5	0.026
175	021913-175A	94.8	470	<2.5	<0.026
	021913-175B	97.8	470	2.5	0.026
	021913-175C	96.9	470	<2.5	<0.026
200	022013-200A	92.3	460	<2.5	<0.027
	022013-200B	94.2	460	3.3	0.035
	022013-200C	94.2	460	2.9	0.031
225*	022113-225A	91.5	450	3.1	0.034
	022113-225B	94.5	450	5.8	0.061
	022113-225C	91.3	450	3.4	0.037
250	022213-250A	91.8	450	<2.5	<0.027
	022213-250B	94.6	450	<2.5	<0.026
	022213-250C	91.1	450	<2.5	<0.028
275	021313-275A	90.6	450	3.9	0.043
	021313-275B	92	450	<2.5	<0.027
	021313-275C	94	450	<2.5	<0.027
300	021213-300A	85.1	420	<2.5	<0.029
	021213-300B	86.1	420	<2.5	<0.029
	021213-300C	84.8	420	<2.5	<0.029
325	020813-325A	85	420	5.9	0.07
	020813-325B	85.2	420	5.2	0.061
	020813-325C	84.7	420	6.4	0.076
350	020713-350A	87.6	420	3.2	0.036
	020713-350B	84.5	420	5	0.059
	020713-350C	64.5	315	3.7	0.057

*=Breakthrough ^=One sample terminated early

Table A-8 Laboratory NIOSH Method 6010 Blanks

SAMPLE ID	TIME (MINUTES)	TOTAL VOLUME (L)	RESULTS (µg)	RESULTS (ppm)
020813-BLK	NA	NA	<2.6	-----
021513-BLK	NA	NA	<2.6	-----
022013-BLK	NA	NA	<2.6	-----
022213-BLK	NA	NA	<2.6	-----

All Particulate cyanide samples <2.5 µg (LOQ).

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